

AD-A135 488

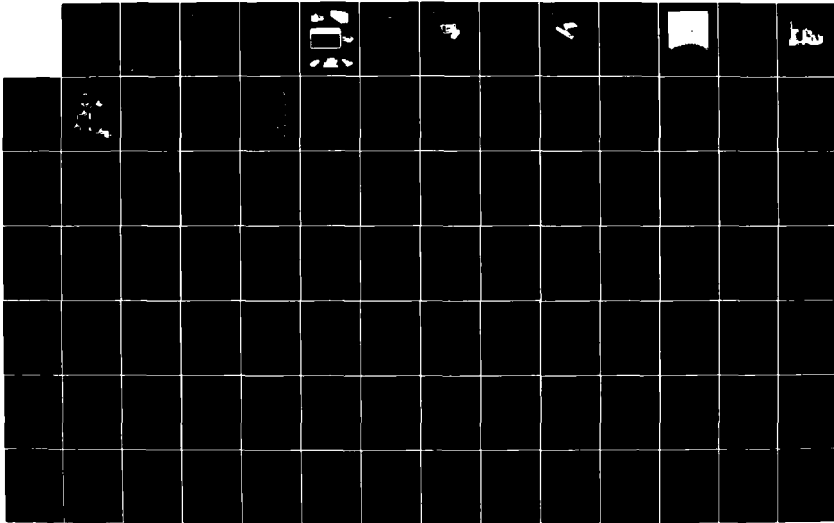
COLLOQUIUM ON HIGH RESOLUTION MOLECULAR SPECTROSCOPY  
(8TH) 19-23 SEPTEMBER (U) EUROPEAN OFFICE OF AEROSPACE  
RESEARCH AND DEVELOPMENT FPO NEW... 23 SEP 83  
EOARD-TR-84-03

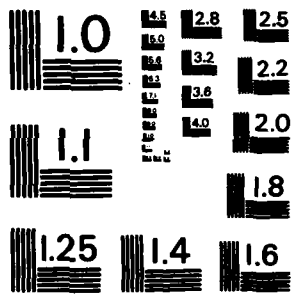
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3

Huitième Colloque

sur la

SPECTROSCOPIE MOLÉCULAIRE  
À HAUTE RÉOLUTION

TOURS

1983

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Eighth Colloquium

on

HIGH RESOLUTION

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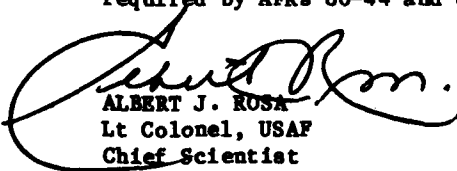
EOARD-TR-84-03, Sep 83, 8th Colloquium on High Resolution Molecular Spectroscopy

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2. DD Form 50

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HUITIÈME COLLOQUE  
SUR LA  
SPECTROSCOPIE MOLÉCULAIRE  
A HAUTE RÉOLUTION

EIGHTH COLLOQUIUM  
ON  
HIGH RESOLUTION  
MOLECULAR SPECTROSCOPY

**TOURS, 1983**

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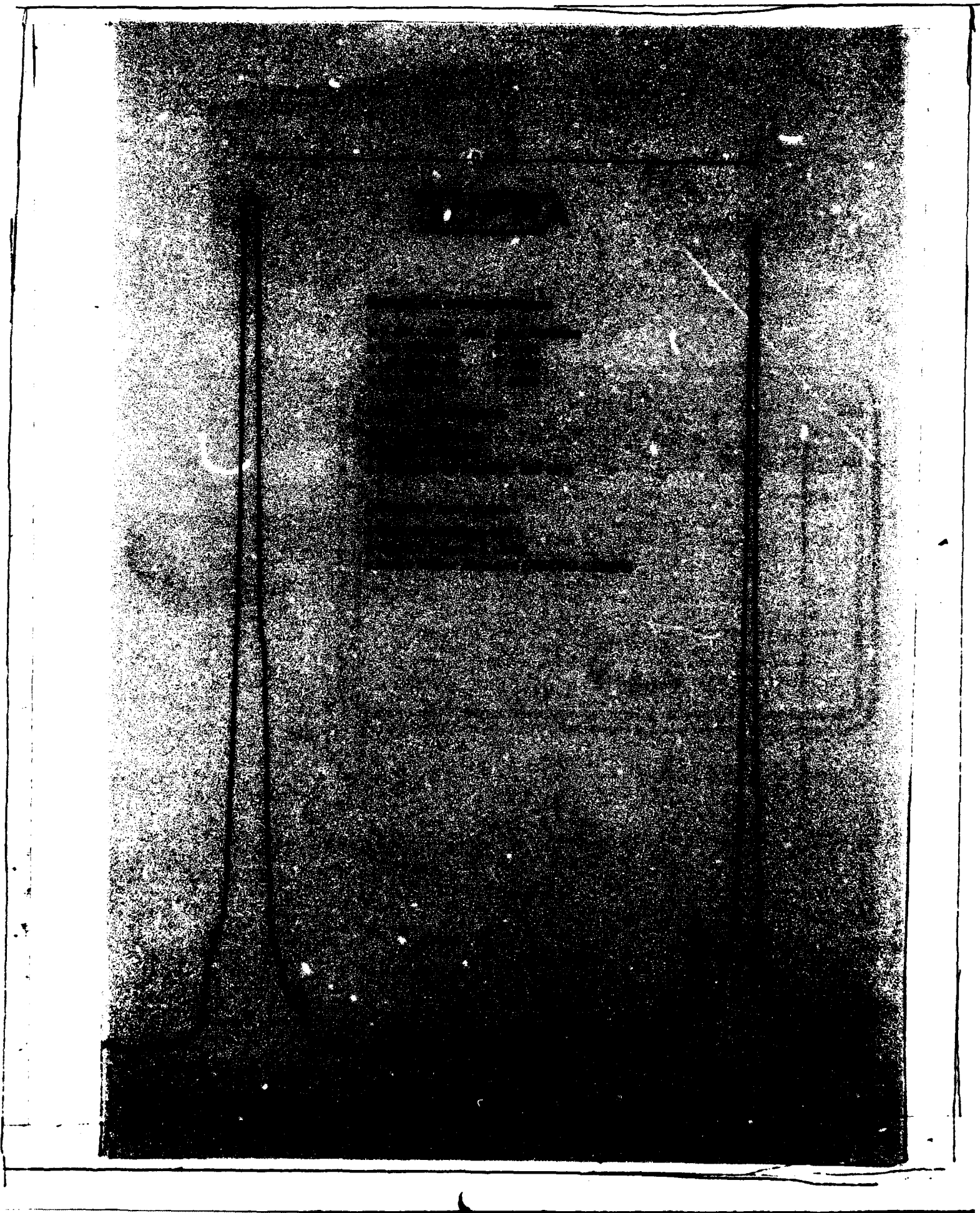
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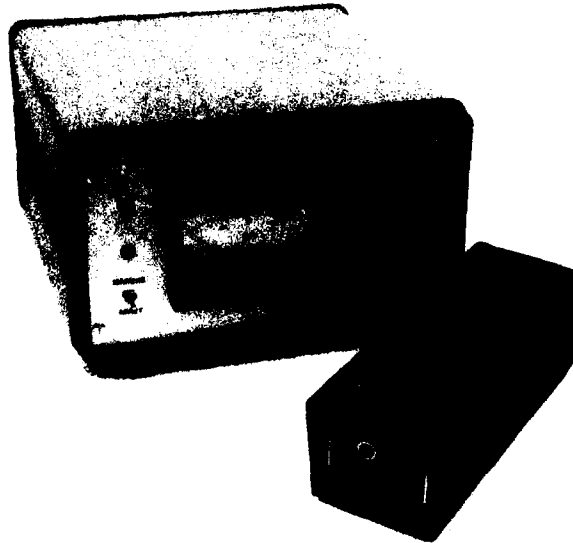


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### LASER CO<sub>2</sub> GUIDE D'ONDE TYPE OL 250

Ce laser fonctionne à 250 milliwatts en mode continu. Il est équipé d'un réseau fixe (émission à 10,59  $\mu$ ) et d'une céramique piezo-électrique (accord de la cavité). De plus, il fonctionne avec ou sans refroidissement par eau.

#### CARACTERISTIQUES

- Puissance de sortie	: 250 milliwatts
- Raie d'émission	: P 20 à 10,59 $\mu$
- Polarisation	: linéaire dans un plan horizontal
- Diamètre du faisceau	: $2 W_0 = 1,28$ mm
- Divergence du faisceau	: 5,2 mrd
- Mode intra-cavité au maximum de puissance	: EH 11
- Mode de propagation hors cavité	: TEM 00
- Largeur de gain à mi-hauteur (FWHM)	: 300 MHz
- Stabilité de fréquence sur une seconde	: < 1 MHz
- Durée de vie	: > 1000 H
- Dimensions de la tête laser avec son capot	: 22 x 7 x 7 cm <sup>3</sup>
- Poids de la tête laser avec son capot	: 1,8 kg
- Dimensions de l'alimentation	: 26 x 15 x 26 cm <sup>3</sup>
- Poids de l'alimentation	: 6 kg.



## WAVE-GUIDE CO<sub>2</sub> LASERS MODEL OL 250

This laser operates at 250 mW power level. It includes a fixed grating which allows an emission at 10.59  $\mu\text{m}$ , and is equipped with bimorph PZT for cavity length control. Moreover, it works with or without water cooling.

### CHARACTERISTICS

- Output power	: 250 mW
- Operational line	: P 20 at 10.59 $\mu\text{m}$
- Polarization	: linear in the horizontal plane
- Beam diameter	: $2 W_0 = 1.28 \text{ mm}$
- Beam divergence	: 5,2 mrd
- Intra cavity mode at maximum power	: EH 11
- Free space mode at maximum power	: TEM 00
- Gain linewidth (FWHM)	: 300 MHz
- Frequency stability in 1 s	: < 1 MHz
- Life time	: > 1000 H
- Laser head dimensions with housing	: 22 x 7 x 7 $\text{cm}^3$
- Weight of laser head with housing	: 1.8 kg
- Power supply dimensions	: 26 x 15 x 26 $\text{cm}^3$
- Weight of power supply	: 6 kg.

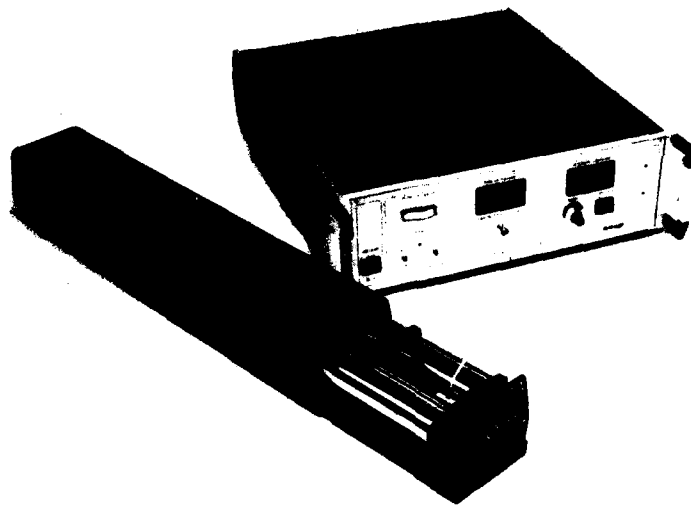


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### LASER CO<sub>2</sub> GUIDE D'ONDE TYPE C 7

Ce laser fonctionne à une puissance comprise entre 5 et 8 watts en mode continu. Il est équipé de fenêtres de BREWSTER (polarisation linéaire horizontale), d'un réseau fixe ou orientable (choix de la longueur d'onde) et d'une électronique de stabilisation automatique en puissance et fréquence.

#### CARACTERISTIQUES

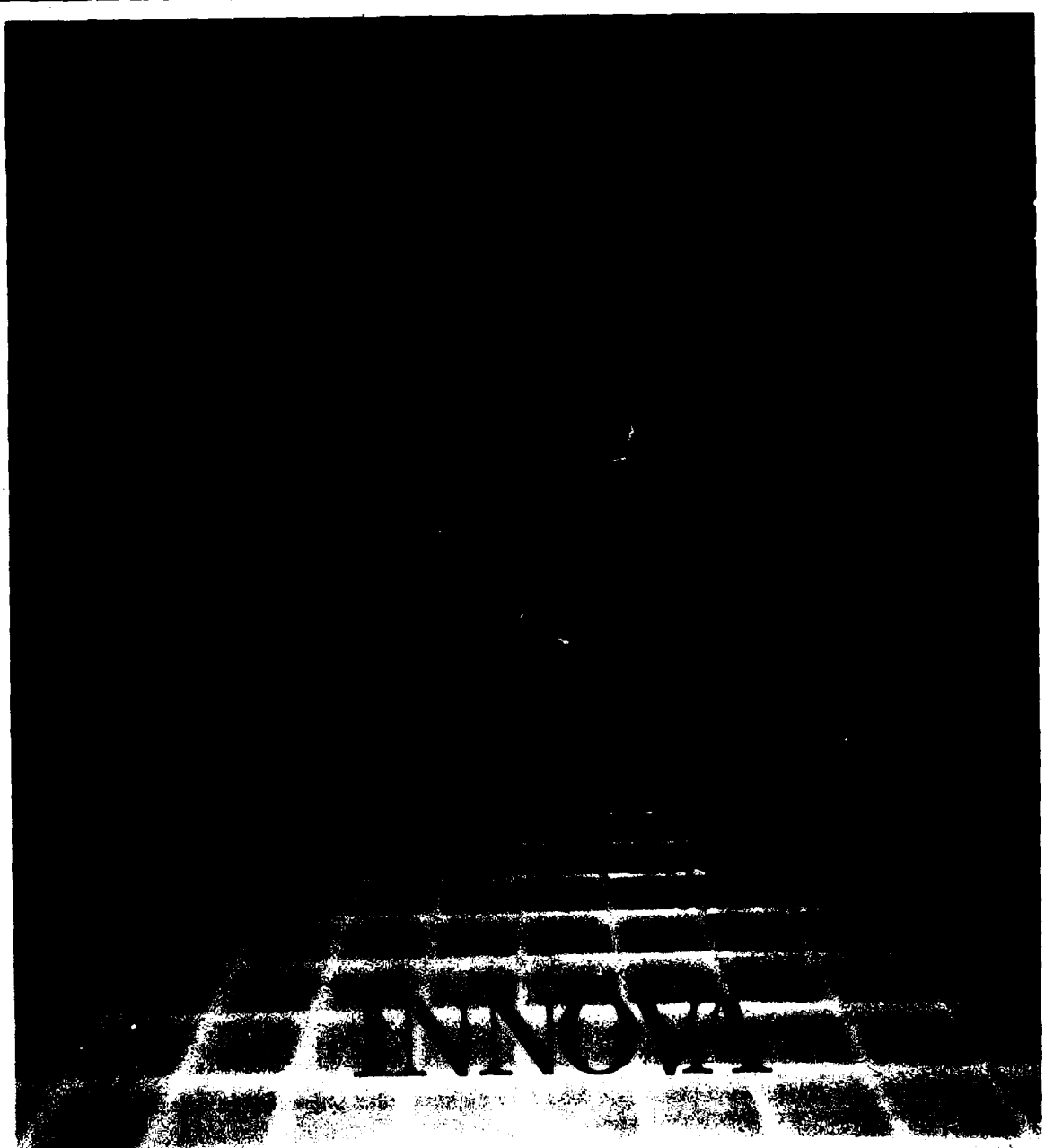
- Puissance de sortie
  - . sur les plus faibles raies : 5 W
  - . sur les plus fortes raies : 8 W
- Raies d'émission autour de 10,6  $\mu$  : P 10 à P 30
- Polarisation : linéaire dans un plan horizontal
- Diamètre du faisceau  $2 W_0 = 2,26$  mm
- Divergence du faisceau : 3,1 mrd
- Mode intra cavité au maximum de puissance : EH 11
- Mode de propagation hors cavité : TEM 00
- Largeur de gain à mi-hauteur (FWHM) : 220 MHz
- Stabilité en fréquence sur une seconde : < 1 MHz
- Durée de vie : > 1000 H
- Refroidissement par eau
- Dimensions de la tête laser avec son capot : 60 x 11 x 11 cm<sup>3</sup>
- Poids de la tête laser avec son capot : 8 kg
- Dimensions de l'alimentation (stabilisation comprise) : 48 x 15 x 50 cm<sup>3</sup>
- Poids de l'alimentation (avec stabilisation) : 20 kg.

## WAVE-GUIDE CO<sub>2</sub> LASERS MODEL C 7

This laser operates at 5 to 8 W power level in continuous mode. It includes, BREWSTER windows for linear horizontal polarization, fixed or tunable grating for the desired wavelength and a feedback control unit for power stabilization.

### CHARACTERISTICS

- Typical output power/in
  - . the weakest lines : 5 W
  - . the strongest lines : 8 W
- Operational lines around 10.6  $\mu\text{m}$  : P 10 to P 30
- Polarization : linear in the horizontal plane
- Beam diameter 2 Wo : 2.26 mm
- Beam divergence : 3.1 mrd
- Intra cavity mode at maximum power : EH 11
- Free space mode at maximum power : TEM 00
- Gain linewidth (FWHM) : 220 MHz
- Frequency stability over 1 s : < 1 MHz
- Life time : > 1000 H
- Cooling : water
- Laser head dimensions with housing : 60 x 11 x 11 cm<sup>3</sup>
- Weight of laser head with housing : 8 kg
- Power supply dimensions with power stabilization : 48 x 15 x 50 cm<sup>3</sup>
- Weight of power supply with power stabilization : 20 kg.



INNOVATION



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L'excellente conductibilité thermique de cette structure " Cool Disk TM " permet l'évacuation instantanée de la chaleur dissipée par la décharge. L'utilisation de disques métalliques élimine les problèmes d'érosion du capillaire tout en assurant une uniformité longitudinale parfaite de la pression de gaz et un rendement optimal.

Les autres caractéristiques essentielles de ce tube sont:

- fenêtres de Brewster en quartz cristallin soudées
- une cathode profilée pouvant dissiper 100 Ampères
- une anode refroidie par conduction et isolée de l'eau pour supprimer les phénomènes d'électrolyse
- un système de remplissage automatique de gaz

la tête laser comprend une cavité en INVAR compensée thermiquement assurant une excellente rigidité et un bon amortissement des vibrations.

L'espace intracavité entre les fenêtres de Brewster et les miroirs est rendu parfaitement étanche à l'aide de composants utilisés en ultravide.

l'alimentation de conception modulaire inclut un boîtier de contrôle à distance.

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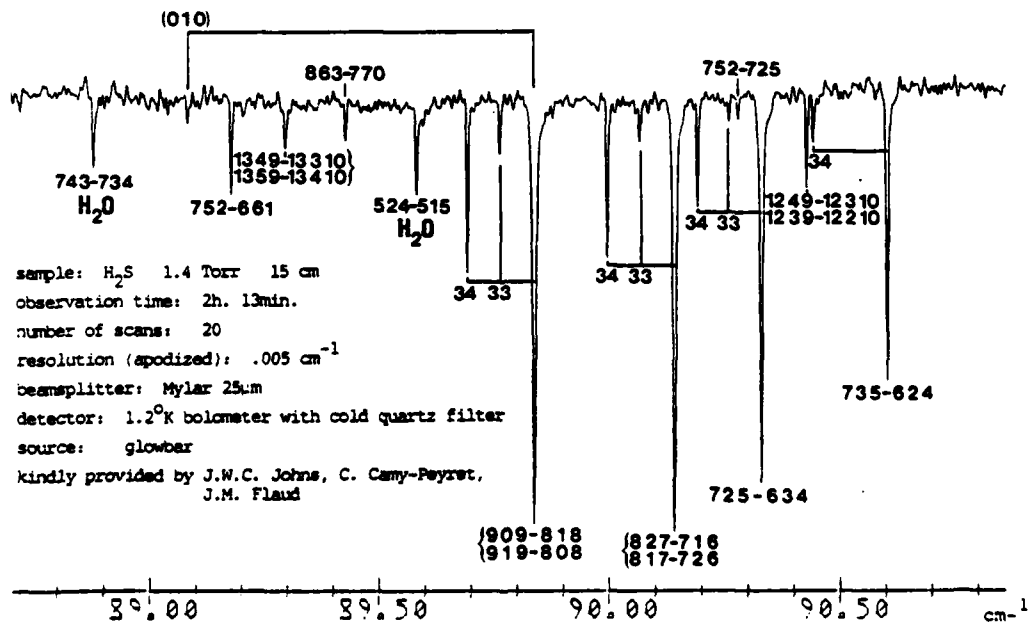
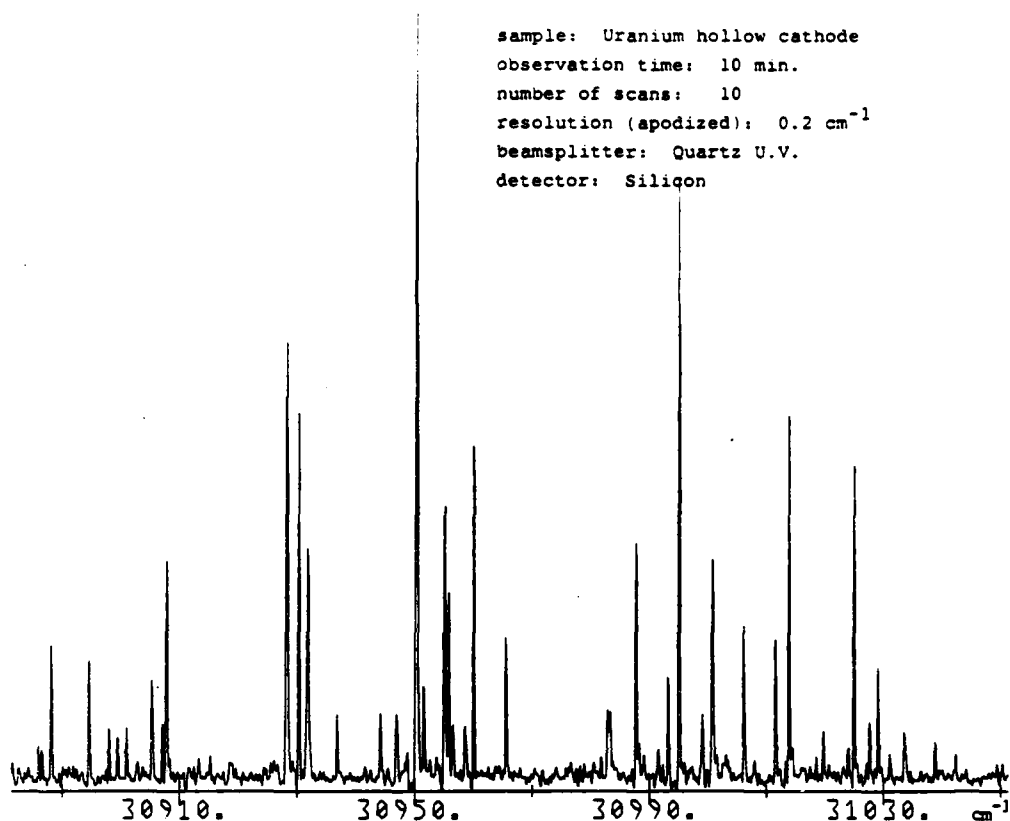


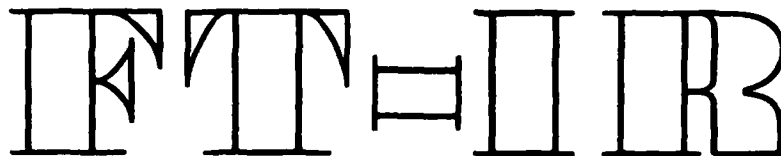
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### INSTRUMAT

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Telex 600 361 INSTRUMAT

sample: Uranium hollow cathode  
 observation time: 10 min.  
 number of scans: 10  
 resolution (apodized):  $0.2 \text{ cm}^{-1}$   
 beamsplitter: Quartz U.V.  
 detector: Silicon





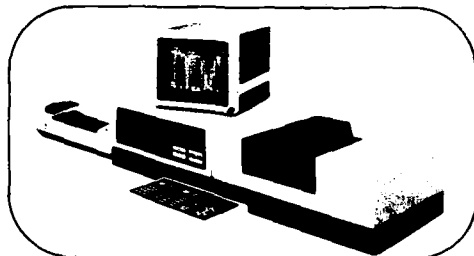
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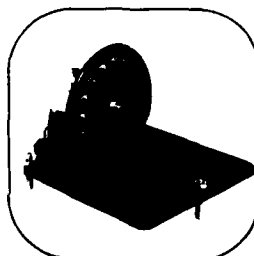
The low cost spectrometer for routine and analytical work

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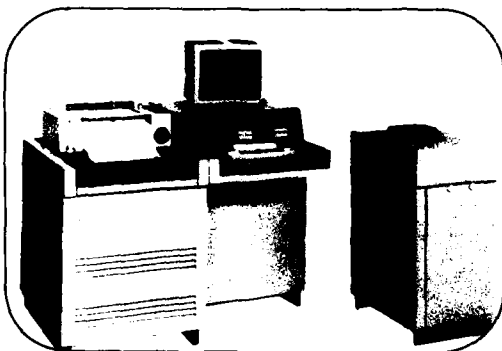
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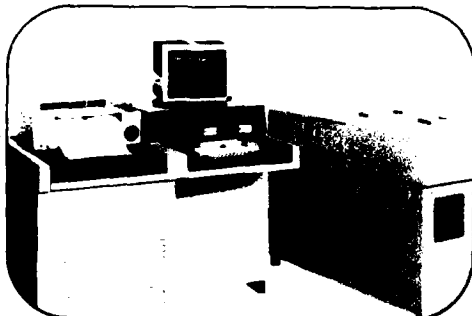
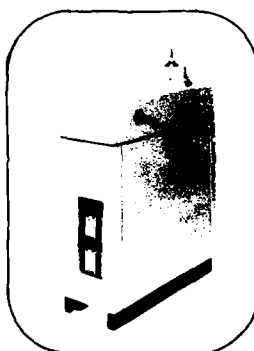
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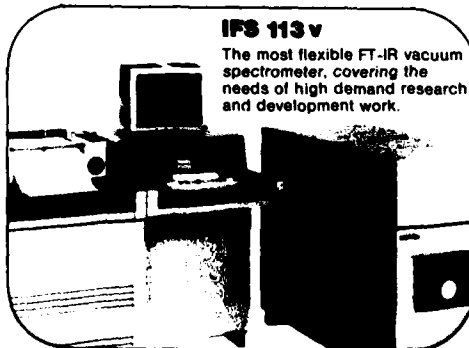
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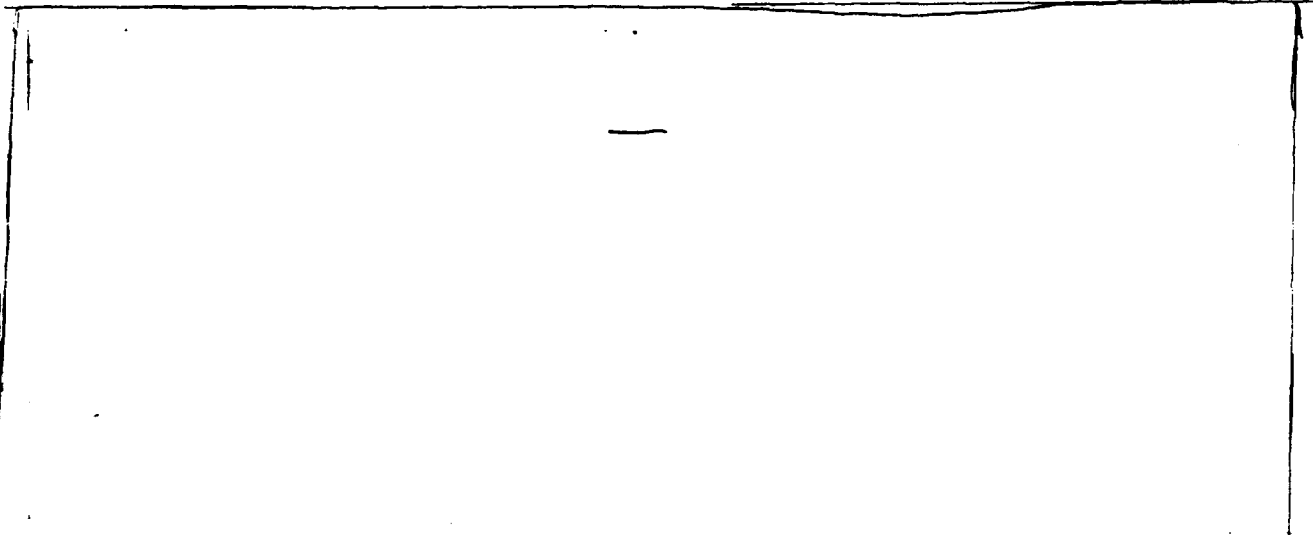
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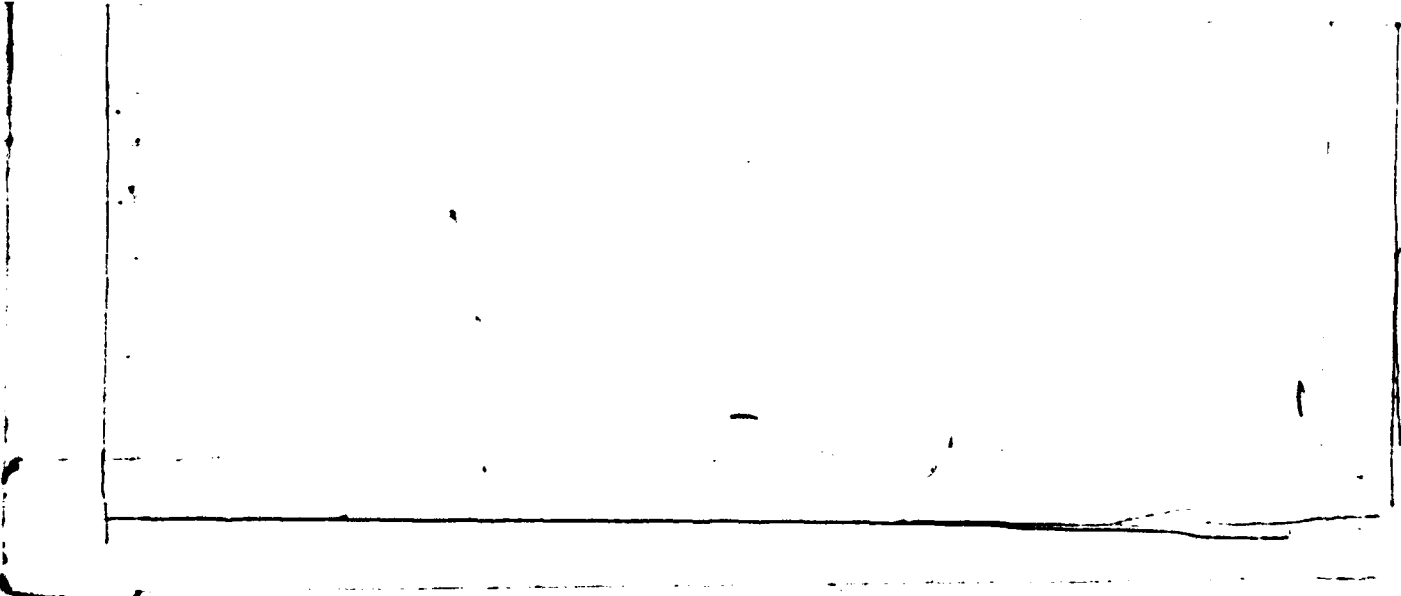
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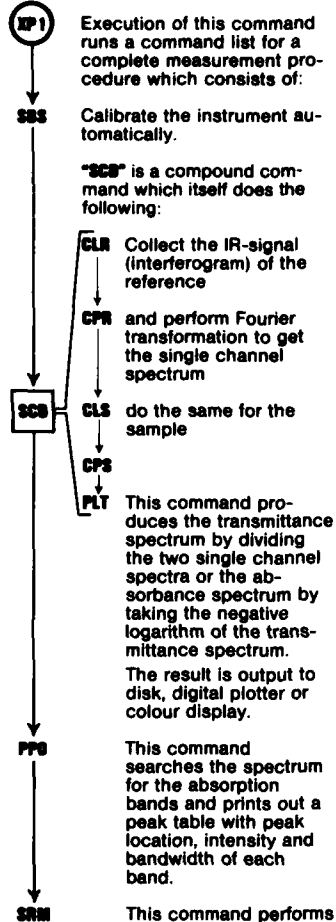
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# From Sample to Identification

A simple three letter command such as "XP1" can do all the following for you within five minutes.



Execution of this command runs a command list for a complete measurement procedure which consists of:

SSS Calibrates the instrument automatically.

"SCS" is a compound command which itself does the following:

GLR Collect the IR-signal (interferogram) of the reference

CPR and perform Fourier transformation to get the single channel spectrum

CLS do the same for the sample

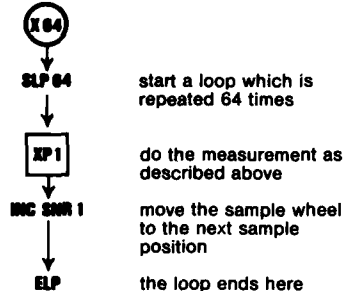
CPS This command produces the transmittance spectrum by dividing the two single channel spectra by taking the negative logarithm of the transmittance spectrum.

The result is output to disk, digital plotter or colour display.

PPO This command searches the spectrum for the absorption bands and prints out a peak table with peak location, intensity and bandwidth of each band.

SRM This command performs a library search through one of the available commercial libraries or one of the user created libraries, prints out the search report and enables the operator to view the full library spectra on the display or digital plotter.

The following example shows how easy it is to do the same for 64 samples using the 64 sample wheel. Again the procedure can be started by a single command such as "XB4"



start a loop which is repeated 64 times

do the measurement as described above

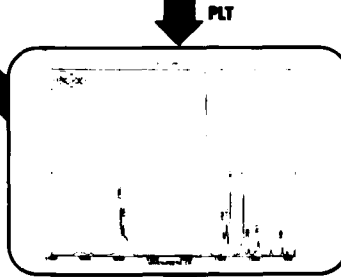
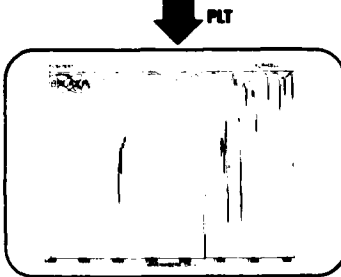
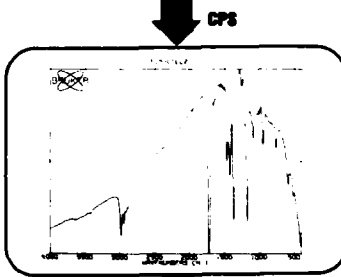
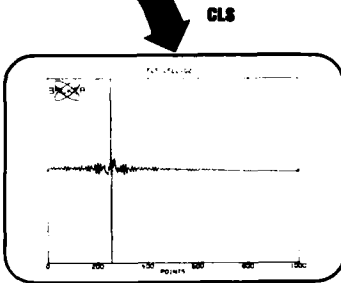
move the sample wheel to the next sample position

the loop ends here

These simple examples which make no use of the automatic timesharing capability can be enhanced by speeding up the whole measurement cycle. This is possible through the powerful "pipelining" feature.

PEAK TABLE FILE 1 SAMPLE

NO.	WAVE-NO.	REL. INTENSITY	WIDTH CM-1
1	590.124	3	12
2	709.846	2	12
3	844.906	6	15
4	1085.74	4	15
5	1172.954	18	15
6	1305.410	10	27
7	1417.479	10	11
8	1459.907	13	27
9	1716.493	100	27
10	2941.027	16	120
11	2979.590	27	27



SEARCH REPORT

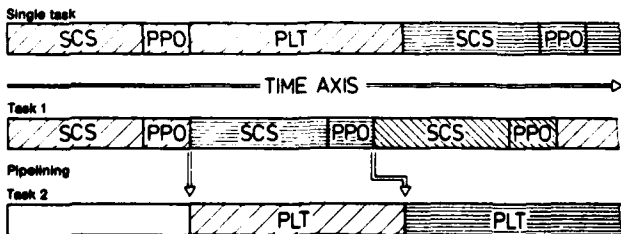
SEARCH IS PERFORMED ON FILE 1 SAMPLE  
 COPYRIGHT ON THE DATA IN THE LIBRARIES IS OWNED BY: ADOLF RESEARCH  
 LABORATORIES. ALL RIGHTS RESERVED. SPECTRA DISPLAYED COPYRIGHT: ADOLF,  
 SÄDLEL VORBEREITUNG LIBRARY. SERIAL NUMBER 1

NO.	HIT QUALITY	SPECTRUM NO	COMPOUND NAME
11	974	3490	BUTANONE
21	750	2814	FORMICACID-BUTYLESTER
31	704	2203	METHYLSULFONE
41	690	99	PENTANONE
51	686	2961	FORMICACID-ISOBUTYLESTER
61	670	4490	HYDROIMIDAZOLIC-2-ETHYL-3-INDOXYL-1-TER
71	647	640	CYCLOPENTEN-3-ONE
81	634	1176	METHANOL-3-METHYL-1
91	624	4917	ALUTRIMIDE-2-1-CYCLOHEXEN-1-YL-2-PROP
101	620	1894	ALUTRIMIDE-2-ACETYL-1-1-ETHYLETHYLESTE

TYPE SPACE FOR DISPLAY OR RETURN FOR EXIT

The pipelining system ensures the most efficient use of computer time.

The following example shows a series of sample measurements with "peak picking" and plotting to digital plotter. In pipelining mode the very time consuming output to digital plotter is executed in a second job region simultaneously with sample measurement and peak picking. The resultant time saving is clearly illustrated in the diagram below.



HUITIEME COLLOQUE

SUR LA SPECTROSCOPIE MOLECULAIRE A HAUTE RESOLUTION

TOURS, 19 - 23 Septembre 1983

***PROGRAMME***

EIGHTH COLLOQUIUM

ON HIGH RESOLUTION MOLECULAR SPECTROSCOPY

TOURS, 19 - 23 September 1983

	Lundi 19 Monday 19	Mardi 20 Tuesday 20	Mercredi 21 Wednesday 21	Jedi 22 Thursday 22	Vendredi 23 Friday 23
Matin	<b>A</b> Bunker Ashfold Guelin	<b>D</b> Hirota Beswick	<b>G</b> Meerts Breyer	<b>K</b> Curl Berger	<b>N</b> Bauder Engelke
		<b>E</b> Poster Session	<b>H</b> Poster Session	<b>L</b> Poster Session	<b>O</b> Poster Session
	<b>B</b> Poster session		<b>I</b> Nall Spirko Lemaire		<b>P</b> Pine
Après-midi	<b>C</b> Poster Session		<b>J</b> Poster Session		<b>Q</b> Poster Session
		<b>F</b> Poster Session	Reception		
Soir				<b>M</b> Carl Merer Tiemann	

Lundi 19 Septembre

9 h 30

*Amphithéâtre*

Monday September 19

9:30

*Auditorium*

CONFERENCES INVITEES

**A**

INVITED LECTURES

- A1** MOLECULES QUASI-LINEAIRES ET QUASI-PLANES. 40 mn  
QUASILINEAR AND QUASIPLANAR MOLECULES.  
P.R. Bunker - Herzberg Institute of Astrophysics, N.R.C, Ottawa,  
Canada, K1A 0R6
- A2** L'IONISATION MULTIPHONIQUE COMME MOYEN D'ETUDE DE LA SPECTROSCOPIE 40 mn  
ET DE LA DYNAMIQUE DES ETATS EXCITES DES PETITES MOLECULES POLYATOMIQUES.  
MULTIPHOTON IONISATION AS A PROBE OF THE SPECTROSCOPY AND DYNAMICS OF  
EXCITED STATES IN SMALL POLYATOMIC MOLECULES.  
M.N.R. Ashfold - Department of Physical Chemistry, Bristol University,  
Cantock's Close, Bristol BS8 1TS, U.K
- A3** SPECTROSCOPIE DE MOLECULES REACTIVES DANS L'ESPACE. 40 mn  
SPACE SPECTROSCOPY OF REACTIVE MOLECULES.  
M. Guélin - I.R.A.M, Domaine universitaire, 38400 Saint-Martin-d'Hères,  
France - Granada, Spain

Lundi 19 Septembre

14 h 30 - 15 h 45

*Gymnase*

Monday, September 19

14:30 - 15:45

*Gymnasium*

POSTER SESSION

**B**

- B1** THE ENERGY DEPENDANCE OF ROTATIONALLY INELASTIC CROSS-SECTIONS AND FITTING LAWS  
B.J. Whitaker, Ph. Bréchnac (Orsay, France)
- B2** INVARIANT PARAMETERS OF THE VIBRATION-ROTATION HAMILTONIAN OF TETRAHEDRAL MOLECULES  
V.G. Tyuterev, V.I. Perevalov (Tomsk, USSR), J.P. Champion, G. Pierre (Dijon, France)
- B3** EXPERIMENTAL AND THEORETICAL ESTIMATE OF TWO-PHOTON INTENSITIES IN THE  $2\nu_2$  BANDS  
OF  $\text{NH}_3$   
A. Di Lieto, P. Minguzzi, S. Profeti, M. Tonelli (Pisa, Italy)

- B4** THE  $\nu_1$  BANDS OF  $^{32}\text{S}^{18}\text{O}_2$  AND  $^{34}\text{S}^{18}\text{O}_2$  FROM IR-MW DOUBLE RESONANCE  
J. Lindenmayer, H. Jones, H.D. Rudolph (Ulm, B.R.D)
- B5** STARK EFFECT STUDIES OF  $\text{CaCl } X^2\Sigma$   
S. Kindt, W.E. Ernst, T. Törring (Berlin, B.R.D)
- B6** ELECTRONIC SPECTRA OF DIATOMIC HALOGEN CATIONS ( $\text{F}_2^+$ ,  $\text{Cl}_2^+$ ,  $\text{Br}_2^+$ )  
 $A^2\Pi_u \rightarrow X^2\Pi_g$   
R.P. Tuckett (Cambridge, U.K)
- B7** ANALYSIS OF THE PERTURBATIONS IN THE INFRARED SPECTRA OBTAINED BY HIGH-RESOLUTION FOURIER SPECTROMETRY :  $^3\Sigma_u^+ - ^3\Pi_g$  INTERACTIONS IN THE  $a^3\Sigma_u^+ \rightarrow a^3\Pi_g$  SYSTEM OF CO MOLECULE AND  $^3\Sigma_g^- - ^1\Sigma_g^+$  INTERACTIONS IN THE  $b^3\Sigma_g^- \rightarrow a^3\Pi_u$  SYSTEM OF  $\text{C}_2$  MOLECULE  
F. Michaud, F. Roux, C. Effantin (Villeurbanne, France); J. Vergès (Orsay, France) ;  
G. Wannous (Beyrouth, Lebanon)
- B8** A FITTING PROCEDURE FOR EXTENSIVELY PERTURBED HAMILTONIANS : APPLICATION TO THE  $A^1\Pi$  STATE OF CO  
A. Le Floch, J. Masson, Ch. Legal (Tours, France)
- B9** THE  $C^2\Pi - X^2\Sigma^+$  TRANSITION OF BO  
H. Bredohl, I. Dubois, F. Melen (Ougrée-Liège, Belgium)
- B10** THE ZEEMAN EFFECT IN THE ORIGIN BAND OF THE  $\tilde{X}^1A_2 + \tilde{X}^1A_1$  SYSTEM OF THIOFORMALDEHYDE  
R.N. Dixon, M.R. Gunson (Bristol, U.K)
- B11** DIRECT  $\ell$ -DOUBLET TRANSITIONS IN THE  $01^1O$  STATE OF CYANOGEN HALIDES  
C. Cazzoli, R. Cervellati, A. Dal Borgo, D.G. Lister, D. Damiani, C. Degli Esposti  
(Bologna, Italy)
- B12** MICROWAVE SPECTRUM OF ACETALDEHYDE IN EXCITED TORSIONAL STATES  
G.C. Petty, J.G. Baker (Manchester, U.K)
- B13** MICROWAVE DOUBLE RESONANCE FOURIER TRANSFORM SPECTROSCOPY  
D.A. Andrews, J.G. Baker (Manchester, U.K)

- B14** THE MOLECULAR STRUCTURE OF AZIDOTRIFLUOROMETHANE,  $CF_3N_3$   
D. Christen, H. Oberhammer (Tübingen, B.R.D)
- B15** THE MICROWAVE SPECTRUM OF PYRROLIDINE  
W. Caminati (Bologna, Italy)
- B16** HIGH RESOLUTION INFRARED SPECTRA OF METHYLENEIMINE  $CH_2NH$  IN THE 3 AND THE 10  $\mu m$  REGIONS  
G. Duxbury (Glasgow, U.K) ; L. Halonen (Espoo, Finland) ; M.L. Le Lerre (Bristol, U.K)
- B17** HIGH RESOLUTION INFRARED SPECTRA OF  $CH_2Cl_2$   
G.D. Nivellini, F. Tullini (Bologna, Italy) ; J.L. Duncan (Old Aberdeen, U.K)
- B18** THE GROUND STATE ROTATIONAL SPECTRUM OF OZONE ( $O_3$ ) BETWEEN 8  $cm^{-1}$  AND 130  $cm^{-1}$ .  
A. Bonetti, E. Carli, F. Forni, F. Mencaraglia (Firenze, Italy) ; M. Carlotti, G. Di Leonardo, L. Fusina, A. Trombetti (Bologna, Italy)
- B19** AIR BROADENED NO LINEWIDTHS IN A TEMPERATURE RANGE OF ATMOSPHERIC INTEREST  
J.P. Houdeau, C. Boulet (Rennes, France) ; J. Bonamy (Besançon, France) ; G. Guelachvili (Orsay, France)
- B20**  $CH_2F_2$  : ANALYSE DU SPECTRE IR VERS 9  $\mu m$ . IDENTIFICATIONS D'EMISSIONS LASERS LIR  
E. Benichou, J.C. Deroche (Orsay, France)
- B21** THE INFRARED SPECTRUM OF THE  $2\nu_9^{\pm 2}$ ,  $\nu_9^{\pm 1} + \nu_{10}^{\pm 1}$ ,  $2\nu_{10}^{\pm 2}$  BAND SYSTEM IN ALLENE- $d_4$   
F. Hegelund, P. Lund (Aarhus, Denmark) ; J.L. Duncan (Old Aberdeen, U.K)
- B22** LINE STRENGTHS ANALYSIS : THE  $\nu_3 - \nu_4$  BAND OF METHANE  
J.C. Hilico, M. Loete, S. Toumi (Dijon, France) ; L.R. Brown (Pasadena, U.S.A)
- B23** NEW DERIVATION OF THE POTENTIAL, SPECTROSCOPIC AND MOLECULAR CONSTANTS OF THE CARBON DIOXIDE FROM ITS INFRARED SPECTRUM  
J.L. Teffo (Paris, France) ; A. Chédin (Palaiseau, France)
-



Lundi 19 Septembre  
16 h 30 - 17 h 45

Monday September 19  
16:30 - 17:45

POSTER SESSION

*Gymnase*

**C**

*Gymnasium*

- C1** THE BENDING COMBINATION STATES OF HCNO  
P. Jensen (Ottawa, Canada) ; B.P. Winnewisser (Giessen, B.R.D)
- C2** GERMYL FLUORIDE : SIMULTANEOUS ANALYSIS OF INFRARED AND MILLIMETER-WAVE SPECTRA OF MONO-ISOTOPIC  $^{74}\text{GeH}_3\text{F}$  AND VIBRATION-ROTATION INTERACTIONS IN EXCITED STATES  
S. Cradock (Edinburgh, U.K)
- C3** THE  $\nu_6$  BAND OF FURTHER ISOTOPIC SPECIES OF  $\text{CF}_2\text{Cl}_2$  FROM IR-MW DOUBLE RESONANCE  
G. Taubmann, H. Jones (Ulm, B.R.D) ; M. Morillon-Chapey (Orsay, France)
- C4** ROVIBRATIONAL LEVELS AND TRANSITION MOMENTS INVOLVED IN THE LASER EMISSION OF  $^{12}\text{CF}_4$  AT 16  $\mu\text{m}$   
G. Poussigue, G. Tarrago (Orsay, France)
- C5** ANALYSIS OF  $^{12}\text{C}_2\text{H}_4$  AND  $^{12}\text{C}^{13}\text{CH}_4$  HOT BANDS IN THE 10  $\mu\text{m}$  REGION  
L. Henry, A. Valentin (Paris, France) ; M. De Vleeschouwer, Ch. Lambeau, A. Fayt (Louvain-la-Neuve, Belgium)
- C6** LES INTENSITES DANS LES BANDES  $\nu_5$  ET  $\nu_8$  DE L'ALLENE  $^{12}\text{C}_3\text{H}_4$   
M. Dang-Nhu (Orsay, France) ; A. Maki, A.S. Pine (Washington D.C, U.S.A)
- C7** LES INTENSITES DANS LES BANDES  $\nu_5$ ,  $\nu_7$  ET  $\nu_8 + \nu_{11}$  DE L'ETHANE  $^{12}\text{C}_2\text{H}_6$   
M. Dang-Nhu (Orsay, France) ; A.S. Pine, W.J. Lafferty (Washington D.C, U.S.A)
- C8** THE MICROWAVE SPECTRUM OF CYANOFORMAMIDE,  $\text{NCCONH}_2$   
J.J. Christiansen (Copenhagen, Denmark)
- C9** THE MICROWAVE SPECTRUM AND STRUCTURE OF CHLOROKETENE  
M.C.L. Gerry, W. Lewis-Bevan, N.P.C. Westwood (Vancouver, Canada)

- C10** MILLIMETER WAVE SPECTROSCOPY OF UNSTABLE SPECIES  
- A DOUBLING SPECTRUM OF THE CH FREE RADICAL  
- ISOTOPIC SUBSTITUTIONS OF CO<sup>+</sup> IN EXCITED VIBRATIONAL STATES  
M. Bogey, C. Demuynck, J.L. Destombes (Villeneuve d'Ascq, France)
- C11** MILLIMETRE WAVE SPECTRUM OF THE C<sub>4v</sub> MOLECULE IODINE OXYGEN PENTAFLUORIDE (IOF<sub>5</sub>)  
P.N. Brier, M.J. Winrow (Manchester, U.K)
- C12** MICROWAVE SPECTRUM OF NITROSOMETHANE WITH ASYMMETRIC CH<sub>2</sub>D AND CHD<sub>2</sub> INTERNAL ROTORS  
D. W. Knight, A.P. Cox (Bristol, U.K)
- C13** THE ELECTRONIC ABSORPTION SPECTRUM OF THE CNO FREE RADICAL IN THE GAS PHASE  
D.A. Ramsay (Ottawa, Canada) ; M. Winnewisser (Giessen, B.R.D)
- C14** DIPOLE MOMENT OF THE FO MOLECULE  
A.R.W. McKellar (Ottawa, Canada)
- C15** FOURIER SPECTROMETRY OF THE LASER INDUCED INFRARED FLUORESCENCE OF Cs<sub>2</sub>  
C. Amiot, C. Crépin, J. Vergès (Orsay, France)
- C16** MESURE DE LA BANDE b<sup>1</sup>Σ<sub>g</sub><sup>+</sup> (v' = 2) X<sup>3</sup>Σ<sub>g</sub><sup>-</sup> (v'' = 0) DE O<sub>2</sub> PAR ABSORPTION INTRACAVITE  
M.A. Mélières, M. Chenevier, F. Stoeckel (Saint-Martin-d'Hères, France)
- C17** STUDY OF THE PREDISSOCIATION OF THE λ<sup>2</sup>Σ<sup>+</sup> STATE OF N<sub>2</sub>O<sup>+</sup> USING HIGH RESOLUTION LASER SPECTROSCOPY  
J. Lermé, S. Abed (Villeurbanne, France) ; R.A. Holt (London, Canada) ;  
M. Larzillière, M. Carré (Villeurbanne, France)
- C18** LASER PREDISSOCIATION SPECTRA OF PH<sub>2</sub><sup>+</sup>  
C.P. Edwards, P.A. Jackson, P.J. Sarre (Nottingham, U.K)
- C19** DOPPLER-FREE TWO PHOTON INFRARED SPECTROSCOPY WITH A FABRY-PEROT RESONATOR  
F. Herlemont, M. Azizi, J. Lemaire (Villeneuve d'Ascq, France)

**C20** RADIATIONLESS TRANSITIONS IN MOLECULES STUDIED BY LASER SATURATION EFFECTS

M. Arnold, F. Bylicki, H.G. Weber, H. Zscheeg (Heidelberg, B.R.D)

**C21** DAY-TIME VARIATION OF ATMOSPHERIC NO<sub>2</sub> FROM HIGH RESOLUTION FOURIER TRANSFORM SPECTRA

J.M. Flaud, C. Camy-Peyret (Orsay, France) ; D. Cariolle (Toulouse, France) ;  
J. Laurent (Chatillon, France) ; G.M. Stokes (Richland, U.S.A)

**C22** DIPOLE STRENGTH AND ELECTRICAL PROPERTIES OF SMALL MOLECULES

M. Gussoni (Genova, Italy) ; C. Castiglioni, P. Jona, G. Zerbi (Milano, Italy)

**C23** QUASI-SYMMETRIC TOP MOLECULE APPROACH TO THE ROTATIONAL-VIBRATIONAL PROBLEM OF CH<sub>3</sub>XY MOLECULES. APPLICATION TO CH<sub>3</sub>C<sup>15</sup>N

J. Koput (Poznan, Poland)

Mardi 20 Septembre  
9 h 00

Tuesday September 20  
9:00

CONFERENCES INVITEES

*Amphithéâtre*

**D**

*Auditorium*

INVITED LECTURES

**D1** SPECTROSCOPIE A HAUTE RESOLUTION D'ESPECES TRANSITOIRES.  
HIGH RESOLUTION SPECTROSCOPY OF TRANSIENT SPECIES.

40 mn

E. Hirota - Institute for Molecular Science, Myodaiji, Okazaki 444 Japan

**D2** ETUDES SPECTROSCOPIQUES DE LA DYNAMIQUE DES MOLECULES DE VAN DER WAALS.  
SPECTROSCOPIC STUDIES OF THE DYNAMICS OF VAN DER WAALS MOLECULES.

40 mn

J.A. Beswick - Laboratoire de Photophysique Moléculaire, Bâtiment 213,  
Université de Paris-Sud, 91405 Orsay Cedex, France

Mardi 20 Septembre  
11 h 15 - 12 h 30

Tuesday September 20  
11:15 - 12:30

POSTER SESSION

*Gymnase*

**E**

*Gymnasium*

- E1** ON DIFFERENT CRITERIONS OF CONSIDERATION OF ANHARMONIC RESONANCES IN TRIATOMIC MOLECULES  
A.Ya. Tsaune (Dnepropetrovsk, USSR) ; V.F. Golovko (Tomsk, USSR)
- E2** ALGEBRAIC MANIPULATIONS WITH VIBRATION-ROTATION IRREDUCIBLE TENSORS  
B.I. Zhilinskii (Moscow, USSR)
- E3** GENERAL AND EXEMPLIFIED THEORY OF RELAXATION  
Th.G. Cats, J.G.M. Kuerten, G. Nienhuis, H.A. Dijkerman (Utrecht, The Netherlands)
- E4** INFRARED-INFRARED DOUBLE RESONANCE OF CH<sub>2</sub>NOH AND CHD<sub>2</sub>F USING AN ACOUSTO-OPTICALLY MODULATED CO<sub>2</sub> LASER  
D. Devoy, G. Duxbury, J. McCombie (Glasgow, U.K)
- E5** QUANTUM BEAT SPECTROSCOPY IN THE B <sup>1</sup>Σ<sup>+</sup> STATE OF MgO  
M. Brieger, H. Büsener, H. Heinrich, A. Hese (Berlin, B.R.D)
- E6** DIFFERENCE FREQUENCY LASER SPECTROSCOPY OF IONS AND FREE RADICALS  
T. Amano (Ottawa, Canada)
- E7** NEW RESULTS FOR UTILIZATION OF THE ATLAS <sup>130</sup>Te<sub>2</sub> RECORDED BY F.T.S  
P. Luc (Orsay, France) ; J. Cariou, Y. Guern, J. Lotrian (Brest, France)
- E8** THE EMISSION SPECTRUM OF THE NCO RADICAL  
M.H. Vervloet (Ottawa, Canada)
- E9** COLLISIONAL ELECTRONIC TRANSFERS IN THE <sup>7</sup>Li<sub>2</sub> MOLECULE  
R. Bacis, B. Barakat, S. Churassy (Villeurbanne, France) ; R.W. Field, C. Linton, S. McDonald (Cambridge, U.S.A) ; F. Martin (Villeurbanne, France) ; J. Vergès (Orsay, France)

- E10** INFRARED FOURIER SPECTROMETRY OF TWO  $^{14}\text{C}$  CONTAINING COMPOUNDS CN AND CO  
C. Amiot, J. Vergès (Orsay, France)
- E11** SPECTROSCOPIC INVESTIGATIONS ON THE COUPLING OF IONIC AND COVALENT STATES OF NaI  
S.H. Schaefer, D. Bender, E. Tiemann (Hannover, B.R.D)
- E12** INFLUENCE OF THE SOURCE FREQUENCY NOISE IN HIGH RESOLUTION SPECTROSCOPY  
F. Rohart, H. Dève, B. Macke (Villeneuve d'Ascq, France)
- E13** MILLIMETER WAVE SPECTRA OF MOLECULES OF ASTROPHYSICAL INTEREST  
D. Boucher, J. Burie, J. Demaison, A. Dubrulle (Villeneuve d'Ascq, France)
- E14** THE STRUCTURE OF  $\text{CF}_3\text{NC}$   
D. Christen, B. Haas, K.J. Ramme, H. Oberhammer (Tübingen, B.R.D)
- E15** MICROWAVE AND MILLIMETER WAVE SPECTRUM OF DIAZIRINE. ROTATIONAL AND HYPERFINE INTERACTIONS ANALYSIS  
M. Bogey, M. Winnewisser (Giessen, B.R.D) ; J.J. Christiansen (Copenhagen, Denmark)
- E16** INTERSTELLAR SEARCH FOR 1-CYANO-BUT-3-EN-1-YNE,  $\text{CH}_2 = \text{CH} - \text{C} \equiv \text{C} - \text{C} \equiv \text{N}$   
H.W. Kroto, D. McNaughton (Brighton, U.K) ; L.T. Little, G.H. McDonald (U.K)
- E17** INFRARED DIODE LASER SPECTROSCOPY OF FREE RADICALS AND IONS  
P.B. Davies, P.A. Hamilton, W.J. Rothwell (Cambridge, U.K)
- E18** HIGH RESOLUTION INFRARED INVESTIGATION OF  $\text{H}_3\text{Si}^{79}\text{Br}$  IN THE  $\nu_2/\nu_5$  REGION NEAR  $950 \text{ cm}^{-1}$   
H. Bürger, H. Beckers (Wuppertal, B.R.D) ; J. Kauppinen (Oulu, Finland)
- E19** THE  $\nu_1$  FUNDAMENTAL BAND OF  $\text{D}_2\text{CO}$  BY DIODE LASER SPECTROSCOPY  
H.J. Clar, K. Yamada, G. Winnewisser (Köln, B.R.D) ; H.P. Gush (Vancouver, Canada)

- E20** THE VISIBLE WATER VAPOR SPECTRUM BETWEEN 13 500 AND 23 000  $\text{cm}^{-1}$   
C. Camy-Peyret, J.M. Flaud, J.Y. Mandin, J.P. Chevillard (Orsay, France) ;  
J.W. Brault (Tucson, U.S.A)
- E21** STRENGTHS AND WIDTHS OF  $\text{N}_2\text{O}$  LINES FROM FOURIER TRANSFORM MEASUREMENTS :  
TEMPERATURE DEPENDENCE OF THE AIR-BROADENING COEFFICIENTS  
A. Lévy, N. Lacombe, G. Guelachvili (Orsay, France)
- E22** TRIDIAGONAL FERMI-RESONANCE STRUCTURE IN THE ISOLATED CH-STRETCHING OVERTONES  
OF FLUORINATED HYDROCARBONS AND  $\text{CD}_3\text{H}$   
H.R. Dübal, M. Lewerenz, M. Quack (Zürich, Switzerland)
- E23** HIGH RESOLUTION INFRARED AND MICROWAVE SPECTRA OF THE HYDROGEN FLUORIDE DIMER  
W.J. Lafferty, A.S. Pine, R.D. Suenram, F.J. Lovas (Washington D.C, U.S.A)

Mardi 20 Septembre  
20 h

Tuesday September 20  
20:00

POSTER SESSION

*Gymnase*

**F**

*Gymnasium*

- F1** HIGH RESOLUTION INFRARED SPECTRA OF  $^{13}\text{C}^{12}\text{CH}_2$  AND  $^{13}\text{C}_2\text{H}_2$  AT 13.7 MICRONS  
J. Hietanen, J. Kauppinen, V.M. Horneman (Oulu, Finland)
- F2** THE  $3\nu_2$  BAND OF  $\text{CH}_3\text{D}$  : ROTATIONAL ANALYSIS, LINE INTENSITIES, AND PRESSURE-  
BROADENING COEFFICIENTS  
B.L. Lutz (Flagstaff, U.S.A)
- F3** INFRARED STUDY OF A  $\text{SiH}_4$  PLASMA AT 5  $\mu$   
P. Chollet, G. Guelachvili, M. Morillon (Orsay, France) ; J.P.M. Schmitt  
(Palaiseau, France)
- F4** THE  $\nu_1$  BAND OF  $^{14}\text{N}^{16}\text{O}_2$  ; LINES POSITIONS AND INTENSITIES  
A. Perrin, J.Y. Mandin, C. Camy-Peyret, J.M. Flaud, J.P. Chevillard,  
G. Guelachvili (Orsay, France)

- F5** INFRARED DOUBLE RESONANCE SPECTROSCOPY OF METHANE AND THE LOCAL MODE MODEL  
A. De Martino, R. Frey, F. Pradère (Palaiseau, France)
- F6** ROVIBRATIONAL SPECTRA OF  $\text{CF}_3^{35}\text{Cl}$  IN THE  $\nu_4$ ,  $2\nu_4$ ,  $3\nu_4$  AND  $\nu_4 + \nu_5$  RANGES  
H. Bürger, R. Grassow (Wuppertal, B.R.D)
- F7** ETUDE DU SPECTRE INFRAROUGE DU SILANE DANS LA REGION DE 830 A 1040  $\text{cm}^{-1}$ .  
ANALYSE DU NIVEAU DE BASE, ET DES NIVEAUX  $\nu_2 = 1$  ET  $\nu_4 = 1$   
G. Pierre (Dijon, France) ; A. Valentin, L. Henry (Paris, France)
- F8** THE MICROWAVE SPECTRUM OF CYANOPHOSPHA-BUTADIYNE  $\text{N} \equiv \text{C} - \text{C} \equiv \text{C} - \text{C} \equiv \text{P}$   
M. Durrant, H.W. Kroto, D. McNaughton, J.F. Nixon (Brighton, U.K)
- F9** MICROWAVE SPECTRUM OF SILYL ACETYLENE IN THE  $3\nu_{10}$  STATE  
A. Bauer, J. Carlier (Villeneuve d'Ascq, France)
- F10** THE MICROWAVE SPECTRUM OF ETHYLAMINE-GAUCHE  
E. Fischer, I. Botskor (Ulm, B.R.D)
- F11** HIGH RESOLUTION ROTATIONAL ZEEMAN EFFECT STUDIES OF SMALL OPEN CHAIN MOLECULES  
D. Hübner, W.H. Stolze, D.H. Sutter (Kiel, B.R.D)
- F12** ROTATIONAL ZEEMAN EFFECT STUDIES OF AROMATIC SYSTEMS  
M. Stolze, W.H. Stolze, D.H. Sutter (Kiel, B.R.D)
- F13** ISOTOPE EFFECTS OF HEAVY ATOMS IN DIATOMIC MOLECULES  
E. Tiemann (Hannover, B.R.D)
- F14** THE SPECTRA OF  $^{74}\text{Ge}^{16}\text{O}$  AND  $^{74}\text{Ge}^{18}\text{O}$  IN THE VACUUM ULTRAVIOLET REGION  
O. Appelblad, A. Lagerqvist, H-ex på Fyl S. Fredin (Stokholm, Sweden)
- F15** ACCURATE MEASUREMENTS OF COLLISIONAL CROSS SECTIONS OF  $\text{BaO} (A^1\Sigma^+)$  WITH Ar  
Th.G. Cats, J.G.M. Kuerten, H.A. Dijkerman (Utrecht, The Netherlands)

- F16** HIGH RESOLUTION UV LASER SPECTROSCOPY OF SH  
W. Ubachs, J.J. ter Meulen, A. Dymanus (Nijmegen, The Netherlands)
- F17**  $\Lambda$ -TYPE DOUBLING AND TERM FORMULAE FOR A  $^5\Pi$  STATE IN THE INTERMEDIATE CASE BETWEEN HUNDS'S CASES (a) AND (b)  
I. Kovacs (Budapest, Hungary)
- F18** SPECTRE DRASC DE  $\text{CO}_2$  A HAUTE TEMPERATURE. RESULTATS EXPERIMENTAUX ET SIMULATION THEORIQUE  
N. Papineau, M. Péalat (Châtillon, France)
- F19** REVISED ANALYSIS OF THE STRUCTURE OF THE  $\nu_1$  BAND OF METHANE BASED ON HIGH RESOLUTION CW CARS SPECTRA  
H. Frunder, D. Illig, H. Finsterhölzl (München, B.R.D) ; H.W. Schrötter  
B. Lavorel, G. Roussel, J.C. Hilico, J.P. Champion, G. Pierre (Dijon, France) ;  
G. Poussigue, E. Pascaud (Orsay, France)
- F20** REALISATION D'UN LAMBDA METRE  
C. Milan, M. Pullicino, G. Roussel, J. Moret-Bailly (Dijon, France)
- F21** COURBES D'ENERGIE POTENTIELLE CALCULEES A LONGUE DISTANCE POUR LES ETATS MOLECULAIRES DES DIMERES ALCALINS  $\text{Li}_2$ ,  $\text{Na}_2$  ET  $\text{K}_2$ , DISSOCIANT EN  $^2S_{1/2} + ^2S_{1/2}$  ET  $^2S_{1/2} + ^2P_J$   
B. Bussery, M. Saute, M. Aubert-Frêcon (Villeurbanne, France)
- F22** GROUP THEORETICAL TREATMENT OF PLANAR INTERNAL ROTATION IN  $(\text{HF})_2$   
J.T. Hougen (Washington D.C, U.S.A)
- F23** ON CALCULATION OF VIBRATION-ROTATION ENERGIES AND POTENTIAL FUNCTION OF DIATOMIC MOLECULES  
V.Ya. Galin (Moscow, USSR) ; V.F. Golovko, Yu.S. Makushkin, V.G. Tyuterev,  
T.I. Velichko (Tomsk, USSR)
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Mercredi 21 Septembre

9 h 00

Wednesday September 21

9:00

*Amphithéâtre*

CONFERENCES INVITEES

**G**

*Auditorium*

INVITED LECTURES

- G1** SPECTROSCOPIE LASER DE MOLECULES DANS LE VIOLET ET L'ULTRAVIOLET : 40 mn  
PETITS RADICAUX ET GROSSES MOLECULES ORGANIQUES.  
LASER SPECTROSCOPY OF MOLECULES IN THE VIOLET AND ULTRAVIOLET REGION :  
SMALL RADICALS AND LARGE ORGANIC MOLECULES.

W.L. Meerts - Fysisch Laboratorium, Katholieke Universiteit, Toernooiveld, Nijmegen, The Netherlands.

- G2** ETATS TRES EXCITES DES PETITES MOLECULES. 40 mn  
HIGHLY EXCITED STATES OF SMALL MOLECULES.

M. Broyer - Laboratoire de Spectrométrie Ionique et Moléculaire, Université de Lyon I, 43 boulevard du 11 Novembre 1918, 69622 Villeurbanne, France.

Mercredi 21 Septembre

11 h 15 - 12 h 30

Wednesday September 21

11:15 - 12:30

*Gymnase*

POSTER SESSION

**H**

*Gymnasium*

- H1** THE EMPIRICAL GENERAL HARMONIC POTENTIAL FUNCTION OF ETHANE  
G.D. Nivellini, F. Tullini (Bologna, Italy) ; J.L. Duncan, R.A. Kelly (Old Aberdeen, U.K)
- H2** ON SOME NEW ASPECTS IN THE KIVELSON-WILSON-NIELSEN THEORY OF VIBRATION-ROTATION STATES OF MOLECULES  
V.N. Bryukhanov, Yu.S. Makushkin, O.V. Naumenko, O.N. Ulenikov (Tomsk, USSR)
- H3** INVERSE RAMAN SPECTROMETER USING A NARROW-LINE WIDTH HIGH-POWER LASER  
B. Lavorel, R. Saint-Loup, R. Chaux, H. Berger (Dijon, France)
- H4** A CW CARS SPECTROMETER WITH INTRACAVITY EXCITATION FOR HIGH RESOLUTION RAMAN SPECTROSCOPY  
H. Frunder, D. Illig, H. Finsterhölzl, K. Fukushi, A. Beckmann, H.W. Schrötter (München, B.R.D)

- H5** AVOIDED-CROSSING EXPERIMENTS IN THE GROUND STATE OF  $\text{NO}_2$  AND  $\text{ClO}_2$   
W. Lienert, W. Majer, H. Häußler, W. Hüttner (Ulm, B.R.D)
- H6** LASER SPECTROSCOPY OF SAMARIUM OXIDE  
P. Carette, A. Hocquet (Villeneuve d'Ascq, France) ; C. Linton (Canada)
- H7** EXPERIMENTAL AND THEORETICAL STUDIES OF POTENTIAL CURVES NEAR DISSOCIATION LIMIT OF THE  $X^1\Sigma_g^+$  AND (1)  $^1\Pi_g$  STATES OF  $\text{Na}_2$   
R.F. Barrow (Oxford, U.K) ; J. Vergès (Orsay, France) ; C. Effantin, K. Hussein, J. d'Incan, B. Bussery, M. Aubert-Frécon (Villeurbanne, France)
- H8** HIGH RESOLUTION EMISSION SPECTRUM OF  $\text{H}_2$  BETWEEN 77 AND 118 nm : MOLECULAR CONSTANTS OF THE  $^1\Pi_u$  STATES  
M. Larzillière (Villeurbanne, France) ; F. Launay (Meudon, France) ; J.Y. Roncin (Saint-Etienne, France)
- H9** STUDY OF THE DISSOCIATION ENERGY OF BN MOLECULE  
S.K. Banumathi (Mysore, India) ; L.S. Gowda (Raichur, India)
- H10** PREDISSOCIATION IN THE  $B^3\Pi_o^+$  STATE OF  $\text{ICl}$   
F. Bäßmann, M. Siese, E. Tiemann (Hannover, B.R.D)
- H11** THE  $r_g$ -STRUCTURE OF s-cis ACROLEIN  
C.E. Blom (Zürich, Switzerland)
- H12** MICROWAVE SPECTRA OF 1, 3, 5-BORADIOXAZINE AND 1, 3, 5-BOROKADIAZINE  
Y. Kawashima, H. Takeo, C. Matsumura (Kanagawa, Japan)
- H13** MICROWAVE SPECTRUM OF METHYL HYDROPEROXIDE ( $\text{CH}_3\text{OOH}$ ) : INTERNAL ROTATION EFFECTS OF METHYL AND HYDROXYL GROUP  
M. Tyblewski, R. Meyer, A. Bauder (Zürich, Switzerland)
- H14** HYPERFINE AND ISOTOPICALLY INVARIANT PARAMETERS OF THE  $\text{GeS}$  MICROWAVE SPECTRUM  
A. Le Floch, J. Masson (Tours, France)
- H15** PREPARATION AND MICROWAVE SPECTRUM OF THE NEW PHOSPHA-ALKENE  $\text{CH}_2 = \text{PCN}$   
M.C. Durrant, H.W. Kroto (Brighton, U.K)

- H16** SPECTRE DE VIBRATION-ROTATION DE LA MOLECULE D'ALLENE DANS LA REGION DE 730 A 1150  $\text{cm}^{-1}$ . DETERMINATION DES NIVEAUX D'ENERGIE ET DES CONSTANTES SPECTROSCOPIQUES ASSOCIEES AUX BANDES  $\nu_9$  ET  $\nu_{10}$   
V. Chazelas, J. Pliva (University Park, U.S.A) ; A. Valentin, L. Henri (Paris, France)
- H17** THE FAR INFRARED SPECTRUM OF HNC0  
M. Carlotti, L. Fusina (Bologna, Italy)
- H18** HIGH RESOLUTION FOURIER AND LASER SPECTROSCOPY OF METHANOL  
G. Moruzzi, F. Strumia (Pisa, Italy)
- H19** THE  $2\nu_2$ ,  $\nu_1$  AND  $\nu_3$  BANDS OF  $\text{H}_2^{32}\text{S}$ ,  $\text{H}_2^{33}\text{S}$  AND  $\text{H}_2^{34}\text{S}$   
L. Fossat, J.M. Flaud, C. Camy-Peyret (Orsay, France) ; J.W.C. Johns (Ottawa, Canada)
- H20**  $^{12}\text{C}^{16}\text{O}^{18}\text{O}$  - ANALYSIS OF EMISSION FOURIER SPECTRA IN THE 4.5  $\mu\text{m}$  REGION : ROVIBRATIONAL TRANSITIONS  $0\nu_2^l \nu_3 - 0\nu_2^l (\nu_3 - 1)$ ,  $\nu_2 = l$   
D. Bailly, C. Rossetti (Orsay, France)
- H21** THE SPECTRUM AND STRUCTURE OF  $\text{CH}_2$  IN THE  $\overset{3}{\chi}^3\text{B}_1$  STATE AND THE ACCURATE DETERMINATION OF THE SINGLET-TRIPLET SPLITTING  
P.R. Bunker (Ottawa, Canada)
- H22** ETUDE DU SPECTRE INFRAROUGE DU SILANE DANS LA REGION DE 2050 A 2300  $\text{cm}^{-1}$ . ANALYSE DES NIVEAUX  $\nu_1 = 1$  ET  $\nu_3 = 1$ .  
P. Lepage, G. Pierre, K. Bouzouba (Dijon, France) ; G. Guelachvili (Orsay, France)
- H23** SUPERHYPERFINE STRUCTURE IN THE  $\nu_3$  BAND OF  $\text{SF}_6$   
J. Bordé, Ch. Bréant, Ch. Salomon, A. Van Lerberghe, Ch.J. Bordé (Villetaneuse, France)
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Mercredi 21 Septembre

14 h

*Amphithéâtre*

Wednesday September 21

14.00 h

*Auditorium*

CONFERENCES INVITEES

I

INVITED LECTURES

- I1 PROGRES RECENTS EN SPECTROSCOPIE LASER A HAUTE RESOLUTION.  
ADVANCES IN HIGH RESOLUTION LASER SPECTROSCOPY 40 mn  
J.L. Hall - Joint Institute for Laboratory Astrophysics,  
Boulder, Colorado 80302, U.S.A
- I2 NH<sub>3</sub> 20 mn  
V. Spirko - J. Heyrovsky Institute of Physical Chemistry and  
Electrochemistry, Flemingovo Nam, 166 10 Prague 6, Czechoslovakia
- I3 RECENTS DEVELOPPEMENTS EN SPECTROSCOPIE LINEAIRE ET EN SPECTROSCOPIE  
LASER A DEUX PHOTONS A L'UNIVERSITE DE LILLE. 20 mn  
RECENTS DEVELOPMENTS IN LINEAR AND TWO-PHOTON LASER SPECTROSCOPY  
AT THE UNIVERSITY OF LILLE.  
J. Lemaire - Laboratoire de Spectroscopie Hertziennne, Université des  
Sciences et Techniques de Lille, Bâtiment P 5, 59655 Villeneuve d'Ascq Cedex,  
France

Mercredi 21 Septembre

16 h 00 - 17 h 15

*Gymnase*

POSTER SESSION

J

Wednesday September 21

16:00 - 17:15

*Gymnasium*

- J1 LINE STRENGTHS ANALYSIS :  $\nu_2$  AND  $\nu_4$  BANDS OF <sup>12</sup>CH<sub>4</sub>  
M. Loete, J.C. Hilico (Dijon, France)
- J2 INTERFERENCE EFFECTS IN THE INFRARED SPECTRUM OF HD AT HIGH PRESSURE  
N.H. Rich, A.R.W. McKellar (Ottawa, Canada)
- J3 SPECTRAL INTENSITIES IN THE  $\nu_5$  BAND OF <sup>12</sup>CD<sub>3</sub>H  
G. Tarrago (Orsay, France) ; F. Cappellani, G. Restelli (Ispra, Italy)

- J4** ROTATIONAL ANALYSIS OF THE  $\nu_2 + \bar{\nu}_4^{\pm 1}$ ,  $\nu_2 + 3\bar{\nu}_6^{\pm 1}$ ,  $\bar{\nu}_4^{\pm 1} + \bar{\nu}_5^{\pm 1}$ ,  $\bar{\nu}_4^{\pm 1} + \bar{\nu}_5^{\pm 1}$ ,  $\bar{\nu}_5^{\pm 1} + 3\bar{\nu}_6^{\pm 1}$ ,  $\bar{\nu}_5^{\pm 1} + 3\bar{\nu}_6^{\pm 1}$ ,  $2\nu_3 + 3\bar{\nu}_6^{\pm 1}$ ,  $\nu_1 + \nu_2$  AND  $\nu_1 + \bar{\nu}_5^{\pm 1}$  INTERACTING INFRARED BANDS OF METHYL CHLORIDE  
N. Ben Sari-Zizi (Rabat, Morocco) ; C. Alamichel (Orsay, France)
- J5** LEAST SQUARES DETERMINATION OF THE TRANSITION DIPOLE MATRIX ELEMENTS FOR  $^{14}\text{NH}_3$  FROM THE LINE INTENSITIES OF THE  $2\nu_2$  AND  $\nu_4$  BANDS  
S. Urban, D. Papousek (Prague, Czechoslovakia) ; V. Malathy Devi (Washington D.C, U.S.A) ; K. Narahari Rao (Columbus, U.S.A)
- J6** SPECTRES VIBRATION-ROTATION DE LA MOLECULE DCP. ENREGISTREMENT DANS LA REGION DE LA FONDAMENTALE  $\nu_2$ , INTERPRETATION DU SPECTRE ET CALCUL DES CONSTANTES SPECTROSCOPIQUES DES ETATS  $01^1_0$ ,  $02^0_0$  ET  $02^2_0$   
J. Lavigne, C. Pépin, A. Cabana (Sherbrooke, Canada)
- J7** PARAMETRES D'ELARGISSEMENT PAR LA PRESSION DE RAIES DE VIBRATION-ROTATION (BANDE  $\nu_3$  DE  $\text{N}_2\text{O}$  ET BANDES FONDAMENTALES DE CO ET DE HBr)  
A. Henry, L. Henry, M.F. Le Moal, M. Margottin-Maclou, B. Seoudi, F. Séverin, A. Valentin (Paris, France)
- J8** ROTATIONAL SPECTRA OF  $^{15}\text{N}$ -LABELED DIAZIRINE ISOTOPOMERS,  $\text{H}_2\text{C} \begin{array}{l} \diagup \text{N} \\ \parallel \\ \diagdown \text{N} \end{array}$   
J. Vogt, M. Winnewisser (Giessen, B.R.D) ; J.J. Christiansen (Copenhagen, Denmark)
- J9** THE MICROWAVE SPECTRUM OF NITROMETHANE AND  $\text{D}_3$ -NITROMETHANE. PRESENT SITUATION  
G.O. Sorensen (Copenhagen, Denmark)
- J10** MICROWAVE SPECTRUM, SUBSTITUTION STRUCTURE AND NORMAL COORDINATE ANALYSIS OF syn-VINYLA LCOHOL  
M. Rodler, C.E. Blom (Zürich, Switzerland)
- J11** ACOUSTIC DETECTION OF MM-WAVE PRESSURE BROADENING  
A. Di Lieto, P. Minguzzi, M. Tonelli (Pisa, Italy) ; M. Meucci (Siena, Italy)
- J12** ROTATION SPECTRA OF EXCITED VIBRATION STATES BY DRM MICROWAVE SPECTROSCOPY  
O.L. Stiefvater (Bangor, U.K)

- J13** EMISSION SPECTRA OF CN IN THE UV AND VUV REGIONS  
K.P. Huber (Ottawa, Canada)
- J14** THE A  $^1\Pi - X^1\Sigma^+$  TRANSITION OF BCl<sub>2</sub>  
H. Bredohl, I. Dubois, Y. Houbrechts, P. Nzohabonayo (Ougrée-Liège, Belgium)
- J15** NEW EMISSION BANDS IN THE HIGH RESOLUTION EMISSION SPECTRUM OF N<sub>2</sub> BETWEEN 85 AND 90 nm  
F. Launay (Meudon, France) ; M. Larzillière (Villeurbanne, France) ;  
J.Y. Roncin (Saint-Etienne, France)
- J16** SPECTROSCOPY OF THE  $^1\Sigma_u^+$  DOUBLE-MINIMUM STATE OF Na<sub>2</sub> FROM THE FOURIER TRANSFORM RECORDS OF THE FLUORESCENCE EXCITED BY SIMPLE AND DOUBLE OPTICAL RESONANCE  
J. d'Incan, C. Effantin, R. Bacis, P. Crozet (Villeurbanne, France) ;  
J. Vergès (Orsay, France) ; R.F. Barrow (Oxford, U.K)
- J17** EVIDENCE OF A STRONG HYPERFINE u-g COUPLING NEAR THE DISSOCIATION LIMIT OF THE B STATE OF I<sub>2</sub>  
J.P. Pique (Saint-Martin-d'Hères, France) ; R. Bacis, S. Churassy (Villeurbanne, France) ; F. Hartmann (Saint-Martin-d'Hères, France) ; J.B. Koffend (Villeurbanne, France)
- J18** POLARIZATION SPECTROSCOPY OF STRONTIUM MONOHALIDE RADICALS  
W.E. Ernst, J.O. Schröder, T. Törring (Berlin, B.R.D)
- J19** LASER STARK SPECTROSCOPY IN PROPYNE : THE  $\nu_5$  PARALLEL BAND  
F. Meyer, J. Dupré, J. Dupré, T. Al Adlouni, C. Meyer (Orsay, France) ;  
J.G. Lahaye, W.K. Ahmed, A. Fayt (Louvain-la-Neuve, Belgium)
- J20** INTRACAVITY SATURATION STARK SPECTROSCOPY OF OCS  
J.G. Lahaye, W.K. Ahmed, P. Stouffs, A. Fayt (Louvain-la-Neuve, Belgium) ;  
J. Lemaire, F. Herlemont (Villeneuve d'Ascq, France)
- J21** CORRELATION DIAGRAMS FOR QUASI-SYMMETRIC TOP MOLECULES WITH A SINGLE ROTOR  
M. Kreglewski (Poznan, Poland)
- J22** THE EMPIRICAL HARMONIC POTENTIAL FUNCTION OF DIBORANE  
J.L. Duncan, J. Harper, E. Hamilton (Old Aberdeen, U.K) ; G.D. Nivellini (Bologna, Italy)

**J23** EXACT ANALYTIC INITIAL VALUES FOR THE DIATOMIC ROTATIONAL HARMONICS

H. Kobeissi (Beyrouth, Lebanon)

Jeudi 22 Septembre

9 h 00

*Amphithéâtre*

Thursday September 22

9:00

*Auditorium*

CONFERENCES INVITEES

**K**

INVITED LECTURES

- K1** SPECTROSCOPIE D'ESPECES TRANSITOIRES AU MOYEN DE LASERS A CENTRES COLORES. 40 mn  
COLOR CENTER LASER SPECTROSCOPY OF TRANSIENT SPECIES.

R.F. Curl - Chemistry Department, Rice University, Houston  
TX 27251, U.S.A

- K2** SPECTROSCOPIE RAMAN NON-LINEAIRE DES GAZ. 40 mn  
NON-LINEAR RAMAN SPECTROSCOPY OF GASES.

H. Berger, J.P. Boquillon - Laboratoire de Spectromie Moléculaire,  
Université de Dijon, 6 boulevard Gabriel, 21 000 Dijon, France

Jeudi 22 Septembre

11 h 15 - 12 h 30

*Gymnase*

Thursday September 22

11:15 - 12:30

*Gymnasium*

POSTER SESSION

- L1** AN ANALYSIS OF FIVE INTERACTING VIBRATIONAL STATES IN  $^{12}\text{CD}_4$   
J.E. Lolck (Aarhus, Denmark) ; E. Pascaud, G. Poussigue (Orsay, France)
- L2** DETERMINATION OF THE CUBIC FORCE FIELD OF NITROSYL FLUORIDE BY VIBRATION-  
ROTATION  $\alpha$  CONSTANTS AND SEXTIC CENTRIFUGAL DISTORTION CONSTANTS  
G. Cazzoli, C. Degli Esposti, P.G. Favero, P. Palmieri (Bologna, Italy)
- L3** UN JEU UNIQUE DE 82 PARAMETRES POUR LE NIVEAU DE BASE, LA DYADE  $\nu_2$  ET  $\nu_5$  ET  
LA PENTADE  $\nu_1, \nu_4, 2\nu_2, \nu_2 + \nu_5$  ET  $2\nu_5$  DE  $^{12}\text{CH}_3\text{F}$   
J.P. Champion, M. Badaoui (Dijon, France)

- L4** USE AND PERFORMANCE IMPROVEMENT OF A COLOUR CENTER LASER FOR SPECTROSCOPY APPLICATIONS  
M. Meucci (Siena, Italy) ; M. Tonelli (Pisa, Italy)
- L5** IR-MW DOUBLE RESONANCE MEASUREMENTS IN TWO LINEAR MOLECULES  
H. Jones (Ulm, B.R.D) ; J. Sheridan (Bangor, U.K)
- L6** RADIOFREQUENCY OPTOGALVANIC SPECTRUM OF  $H_2$  IN THE 700 nm - 780 nm REGION  
M.C. Curtis, P.J. Sarre (Nottingham, U.K)
- L7** THE DESLANDRES-D'AZAMBUJA SYSTEM OF  $^{13}C_2$  MOLECULE  
A. Antic-Jovanovic, V. Bojovic (Belgrade, Yugoslavia)
- L8** LABORATORY AND ASTROPHYSICAL DETERMINATIONS OF THE RADIATIVE LIFETIME OF  $CH^+$  ( $A^1\Pi$  ;  $v = 0$ )  
M.N. Dumont, N. Grevesse, F. Rémy (Liège-Ougrée, Belgium) ; J. Sauval (Bruxelles, Belgium)
- L9** THE TRIPLET SYSTEM ( $A^3\Pi - X^3\Pi$ ) OF BN  
H. Bredohl, I. Dubois, Y. Houbrechts, P. Nzohabonayo (Ougrée-Liège, Belgium)
- L10** THE SINGLET BANDS OF BN  
H. Bredohl, I. Dubois, Y. Houbrechts, P. Nzohabonayo (Ougrée-Liège, Belgium)
- L11** THE DIPOLE MOMENT OF THIOFORMALDEHYDE IN ITS SINGLET AND TRIPLET  $\pi^{\ast}$ - $n$  EXCITED STATES  
R.N. Dixon, M.R. Gunson (Bristol, U.K)
- L12** NEW DEVELOPMENTS IN MICROWAVE FOURIER TRANSFORM SPECTROSCOPY  
G. Bestmann, H. Dreizler, E. Fliege, W. Kasten, H. Mäder, W. Stahl (Kiel, B.R.D)
- L13** HIGH RESOLUTION MICROWAVE SPECTRUM OF PROPYLFLUORIDE  
W. Kasten, H. Dreizler (Kiel, B.R.D)



- L14** ROTATIONAL RELAXATION STUDIES BY MICROWAVE SPECTROSCOPY  
H. Mäder, H. Bomsdorf, W. Schrepp (Kiel, B.R.D)
- L15** PRESSURE AND LINEWIDTH MEASUREMENTS OF THE PURE ROTATION RAMAN SPECTRA OF NITROGEN AND OXYGEN  
H.G.M. Edwards, D.A. Long, S.W. Webb (Bradford, U.K)
- L16** SPECTRES MICROONDE DE SF<sub>5</sub>Cl DANS LES ETATS EXCITES  $\nu_6(B_1) = 1$  ET  $\nu_{11}(E) = 1$   
P. Goulet, R. Jurek, C. Verry (Dijon, France)
- L17** ANALYSIS OF THE HIGH-RESOLUTION CARS SPECTRUM OF THE Q-BRANCH OF THE  $\nu_1$  BAND OF AMMONIA  
H. Frunder, H. Finsterhölzl, H.W. Schrötter (München, B.R.D) ; S. Urban, D. Papousek (Prague, Czechoslovakia)
- L18** DIODE LASER SPECTRA OF ETHYLENE IN THE 11.8  $\mu\text{m}$  REGION  
M. de Vleeschouwer, Ch. Lambeau, A. Fayt (Louvain-la-Neuve, Belgium) ; Ph. Herbin, J. Walrand, G. Blanquet, C.P. Courtoy (Namur, Belgium)
- L19** THE  $\nu_2$ ,  $2\nu_2 - \nu_2$  AND  $\nu_4$  BANDS OF ND<sub>3</sub>  
G. Di Lonardo, L. Fusina (Bologna, Italy)
- L20** FLUOROFORM : ANALYSIS OF THE 8-9 MICRONS POLYAD  
G. Graner, G. Guelachvili (Orsay, France)
- L21** ANALYSE DE LA TRANSITION  $\nu_3 - \nu_1$  DU DISULFURE DE CARBONE A PARTIR DE SPECTRES OBTENUS A L'AIDE D'UN SPECTROMETRE A GRILLES ET D'UN SPECTROMETRE A DIODE-LASER  
E. Baeten, Gh. Blanquet, Ph. Herbin, J. Walrand, C.P. Courtoy (Namur, Belgium)
- L22** ANALYSE DES BANDES  $\nu_2 + \nu_3^{\pm 1}$  ET  $\nu_1 + \nu_2$  DE <sup>14</sup>NH<sub>3</sub>  
M.L. Grenier-Besson, V. Dana (Paris, France) ; J.P. Maillard (Meudon, France)
- L23** ROVIBRATIONAL ANALYSIS OF THE  $\nu_7$  IN DIAZIRINE : H<sub>2</sub>C  $\begin{matrix} \text{N} \\ \parallel \\ \text{N} \end{matrix}$   
A. Gambi (Giessen, B.R.D)
-

Jeudi 22 Septembre

20 h 00

*Amphithéâtre*

Thursday September 22

20:00

*Auditorium*

CONFERENCES INVITEES

**M**

INVITED LECTURES

- M1** SPECTROSCOPIE A HAUTE RESOLUTION DE L'EMISSION STRATOSPHERIQUE  
DANS LA REGION SUBMILLIMETRIQUE. 30 mn  
HIGH RESOLUTION SPECTROSCOPY OF THE STRATOSPHERIC EMISSION IN  
THE SUBMILLIMETER REGION.

B. Carli - Istituto di Recerca Sulle Onde Elettromagnetiche del  
C.N.R., Via Panciatichi 64, 50127 Firenze, Italy

- M2** PROGRES RECENTS EN SPECTROSCOPIE DES OXYDES DE METAUX DE TRANSITION  
3 d. 30 mn  
RECENT PROGRESS IN THE SPECTROSCOPY OF THE 3 d TRANSITION METAL OXIDES.

A.J. Merer - Department of Chemistry, University of British Columbia,  
2036 Main Mall, Vancouver, B.C, Canada V6T 1Y6

- M3** EFFETS ISOTOPIQUES D'ATOMES LOURDS DANS DES MOLECULES DIATOMIQUES.  
ISOTOPE EFFECTS OF HEAVY ATOMS IN DIATOMIC MOLECULES. 30 mn

E. Tiemann - Institut für Atom-und Molekülphysik, Abteilung Spektroskopie,  
Universität Hannover, Appelstrasse 2, 3 000 Hannover 1, B.R.D

Vendredi 23 Septembre

9 h 00

*Amphithéâtre*

Friday September 23

9:00

*Auditorium*

CONFERENCES INVITEES

**N**

INVITED LECTURES

- N1** ETAT ACTUEL DE LA SPECTROSCOPIE MICROONDES PAR TRANSFORMEE DE  
FOURIER. 40 mn  
PRESENT STATE OF MICROWAVE FOURIER TRANSFORM SPECTROSCOPY

A. Bauder - Eidg. Technische Hochschule, Laboratorium für  
Physikalische Chemie, 8092 Zürich, Switzerland

- N2** SPECTROSCOPIE A HAUTE RESOLUTION PAR FAISCEAU LASER ET JET  
MOLECULAIRE CROISES : QUO VADIS ?  
HIGH RESOLUTION CROSSED LASER-MOLECULAR BEAM SPECTROSCOPY :  
QUO VADIS ?

40 mn

F. Engelke - Fakultät für Physik, Universität Bielefeld,  
Postfach 8640, 4800 Bielefeld 1, B.R.D

Vendredi 23 Septembre  
11 h 15 - 12 h 30

Friday September 23  
11:15 - 12:30

POSTER SESSION

*Gymnase*



*Gymnasium*

- O1** PREDICTIONS FOR MAGNETIC DIPOLE TRANSITIONS IN THE GROUND STATE OF SF<sub>6</sub>  
M.L. Palma (Paris, France) ; N. Macias Marques (Lisboa, Portugal) ; J. Bordé  
(Villetaneuse, France)
- O2** APPLICATION OF DIRECT NUMERICAL DIAGONALIZATION TECHNIQUES TO LINEAR TRIATOMIC  
MOLECULES  
R.B. Wattson (Burlington, U.S.A) ; L.S. Rothman (Hanscom AFB, U.S.A)
- O3** NONADIABATIC CONTRIBUTIONS TO THE DIPOLE MOMENTS OF <sup>7</sup>LiH AND <sup>7</sup>LiD IN THE  
A <sup>1</sup><sub>2</sub><sup>+</sup> STATE  
M. Brieger, A. Renn, A. Hese (Berlin, B.R.D)
- O4** MULTIPHOTON IONISATION SPECTROSCOPY OF H<sub>2</sub>O AND H<sub>2</sub>S  
M.N.R Ashfold, J.M. Bayley, R.N. Dixon (Bristol, U.K)
- O5** LASER MAGNETIC RESONANCE ROTATIONAL SPECTROSCOPY OF <sup>2</sup>Σ RADICALS : ETHYNYL (CCH)  
R.J. Saykally, L. Veseth (Berkeley, U.S.A) ; K.M. Evenson (Boulder, U.S.A)

- O6** DYNAMICS OF IR-MULTIPHOTON EXCITATION OF POLYATOMIC MOLECULES FROM HIGH RESOLUTION SPECTROSCOPY  
M. Quack, G. Seyfang, E. Sutcliffe (Zürich, Switzerland)
- O7** LASER PREDISSOCIATION SPECTRUM OF  $\text{PH}^+$  ( $A^2\Delta + X^2\Pi$ ). RESOLUTION OF PROTON AND  $^{31}\text{P}$  HYPERFINE STRUCTURE  
C.P. Edwards, P.A. Jackson, C.S. Maclean, P.J. Sarre (Nottingham, U.K) ;  
D.J. Milton (Coventry, U.K)
- O8** HIGH RESOLUTION ANALYSIS OF THE BENDING VIBRATIONAL MODE TRANSITIONS IN THE  $\tilde{A}-\tilde{X}$  SPECTRUM OF  $\text{N}_2\text{O}^+$   
S. Abed, J. Lermé, M. Larzillière, M. Carré (Villeurbanne, France)
- O9** NEW LASER INDUCED FLUORESCENCE FOURIER TRANSFORM SPECTROMETRY : EXPLORATION OF THE  $\text{Li}_2$  MOLECULE  
J. Vergès (Orsay, France) ; R. Bacis, B. Barakat, S. Churassy, P. Crozet (Villeurbanne, France)
- O10** FOURIER SPECTROSCOPY OF THE  $^{13}\text{C}_2$  AND  $^{12}\text{C}^{13}\text{C}$  PHILLIPS, BALLIK-RAMSAY AND SWAN ELECTRONIC SYSTEMS  
C. Amiot, J. Vergès (Orsay, France)
- O11** INVESTIGATIONS OF PERTURBED STATES OF  $\text{BaO}$  BY UV-LASERSPECTROSCOPY  
D. Bender, S.H. Schaefer, E. Tiemann (Hannover, B.R.D)
- O12** EMISSION SPECTRUM ASSIGNED TO HCCS  
B. Coquart (Reims, France) ; M. Vervloet (Ottawa, Canada)
- O13** MICROWAVE SPECTRA AND NORMAL COORDINATE ANALYSIS OF  $\text{F}_2\text{C}-\text{N}-\text{CF}_3$   
H. Günther (Karlsruhe, B.R.D) ; K. Ramme, G. Schrem (Tübingen, B.R.D)
- O14** MILLIMETER WAVE SPECTRUM OF  $^{17}\text{O}_2$ . MAGNETIC HYPERFINE STRUCTURE AND QUADRUPOLE COUPLING CONSTANTS  
G. Cazzoli, C. Degli Esposti, P.G. Favero (Bologna, Italy) ; B.M. Landsberg (Bangor, U.K)

- O15** POPULATION INVERSION BETWEEN  $\Lambda$  DOUBLING LEVELS OF OH : EXPERIMENTAL EVIDENCE FOR THE INVERTING ROLE OF THE H-OH COLLISIONS  
M. Bogey, C. Demuyck, J.L. Destombes (Villeneuve d'Ascq, France)
- O16** INVERSE LAMB DIP SPECTROSCOPY USING MICROWAVE SIDEBANDS OF CO<sub>2</sub> LASER LINES  
G. Magerl, J.M. Frye, W.A. Kreiner, T. Oka (Chicago, U.S.A)
- O17** DIODE LASER SPECTROSCOPY OF THE  $\nu_3$  BANDS OF CF<sub>2</sub> AND NF<sub>2</sub>  
P.B. Davies, P. Hamilton (Cambridge, U.K) ; D.K. Russell (Leicester, U.K)
- O18** HIGH RESOLUTION SPECTRUM OF THE  $\nu_4$  BAND OF CD<sub>3</sub>I  
R. Anttila, M. Koivusaari (Oulu, Finland) ; G. Guelachvili (Orsay, France)
- O19** DIODE LASER SPECTROSCOPY WITH A MULTIPLE REFLECTION DISCHARGE CELL  
W. Klebsch, K. Yamada, G. Winnewisser (Köln, B.R.D)
- O20** ANOMALOUS CENTRIFUGAL DISTORTION EFFECTS IN NON RIGID MOLECULES : THE WATER MOLECULE  
V.I. Starikov, V.I. Tolmachev, V.G. Tyuterev (Tomsk, USSR) ; J.M. Flaud, C. Camy-Peyret (Orsay, France)
- O21** LINE PROFILE IN THE INFRARED SPECTRUM OF N<sub>2</sub>O  
N. Lacome, A. Lévy (Orsay, France) ; Ch. Boulet (Rennes, France)
- O22** PURE ROTATIONAL RAMAN SPECTRA OF ETHYLENE ISOTOPIC DERIVATIVES  
F.J. Mompean, R. Escribano (Madrid, Spain)
- O23** LABORATORY SPECTROSCOPY PROGRAMME AT RAL. DESCRIPTION AND SOME INITIAL RESULTS  
J. Ballard, W.B. Johnston, P.F. Gray, P.H. Moffat, D.T. Llewellyn-Jones, J.E. Harries (Didcot, U.K)
-

Vendredi 23 Septembre  
14 h 00

Friday September 23  
14:00

*Amphithéâtre*

CONFERENCE INVITEE  
**P**  
INVITED LECTURE

*Auditorium*

**P1**

PREDISSOCIATION VIBRATIONNELLE ET EFFET TUNNEL POUR LES  
DIMERES (HF)<sub>2</sub> ET (DF)<sub>2</sub>.  
VIBRATIONAL PREDISSOCIATION AND TUNNELLING IN THE HYDROGEN  
FLUORIDE DIMER (HF)<sub>2</sub> AND (DF)<sub>2</sub>.

30 mn

A.S. Pine, W.J. Lafferty - Molecular Spectroscopy Section 23240  
National Bureau of Standards, Washington D.C, 20234, U.S.A

Vendredi 23 Septembre  
15 h 00 - 16 h 15

Friday September 23  
15:00 - 16:15

*Gymnase*

POSTER SESSION  
**Q**

*Gymnasium*

**Q1**

MICROWAVE SPECTRA OF EXCITED STATES OF CYCLOBUTYLSILANE  
A. Wurstner-Rueck, H.D. Rudolph (Ulm, B.R.D)

**Q2**

DETERMINATION OF SPECTROSCOPIC CONSTANTS FOR THE A<sup>2</sup>Π-STATE OF Na-Ar BY  
LASER-SPECTROSCOPY  
G. Aepfelbach, A. Nunnemann, D. Zimmermann (Berlin, B.R.D)

**Q3**

STRUCTURE OF KCN, NaCN, AND LiNC BY MOLECULAR BEAM ELECTRIC RESONANCE  
SPECTROSCOPY  
J.J. van Vaals, W.L. Meerts, A. Dymanus (Nijmegen, The Netherlands)

**Q4**

LASER-STARK ANALYSIS OF THE ν<sub>2</sub> AND ν<sub>5</sub> BANDS OF SiH<sub>3</sub>F  
R. Escribano (Madrid, Spain) ; R.J. Butcher (Cambridge, U.K)

**Q5**

PERTURBATION AND PREDISSOCIATION EFFECTS IN THE A<sup>3</sup>Π STATE OF THE SH<sup>+</sup>  
AND SD<sup>+</sup> IONS  
M. Horani, J. Rostas (Orsay, France) ; J. Brion, D. Daumont, J. Malicet  
(Reims, France)

- Q6** VIBRATIONAL-ROTATIONAL ANALYSIS OF THE INFRARED FUNDAMENTALS  $\nu_5, \nu_6, \nu_8$  AND  $\nu_9$  OF DIAZOMETHANE  
L. Nemes (Budapest, Hungary) ; J. Vogt, M. Birk, M. Winnewisser (Giessen, B.R.D)
- Q7** RADIATIVE LIFETIME MEASUREMENTS IN ION PAIR STATES OF  $I_2$   
B. Femelat, J.P. Perrot, J. Chevaleyre, M. Broyer (Villeurbanne, France)
- Q8** OPTICAL-OPTICAL DOUBLE RESONANCE IN  $I_2$  WITH AN U.V. CONTINUOUS WAVE LASER  
J.P. Perrot, A. Bouvier, J. Chevaleyre (Villeurbanne, France)
- Q9** LASER EXCITED FLUORESCENCE SPECTRA OF  $^{39}K^6Li$  AND  $^{39}K^7Li$   
F. Engelke, H. Hage, U. Sprick (Bielefeld, B.R.D)
- Q10** DOPPLER-FREE TWO PHOTON IONIZATION CROSSED LASER-MOLECULAR BEAM SPECTROSCOPY : THE  $K_2 B^1\Pi_u - X^1\Sigma_g^+$  BAND SYSTEM  
F. Engelke, H. Hage, U. Schüle (Bielefeld, B.R.D)
- Q11** COLLISION INDUCED TRANSITIONS IN ROTATIONAL MANIFOLD OF OCS PERTURBED BY Ar, He AND  $H_2$   
A. Picard-Bersellini, B.J. Whitaker (Orsay, France)
- Q12** HOW GENERAL IS THE CONCEPT OF EFFECTIVE ROTATIONAL HAMILTONIANS FOR OPEN-SHELL DIATOMICS ?  
J. Schlembach, E. Tiemann (Hannover, B.R.D)
- Q13** VIBRATION-ROTATION SPECTRA OF OCS AND  $CO_2$  BELOW  $900\text{ cm}^{-1}$   
K. Jolma, J. Kauppinen, V.M. Horneman (Oulu, Finland)
- Q14** GLYOXAL SPECTROSCOPY BY ENERGY LEVEL ANTICROSSINGS IN STRONG MAGNETIC FIELD  
P. Dupré, R. Jost, M. Lombardi, C. Michel (Saint-Martin-d'Hères - Grenoble, France)
- Q15**  $CO_2$  LASER FREQUENCY STABILIZATION BY EXTERNAL DOPPLER DITHER MODULATION  
G. Magerl, W. Schupita (Wien, Austria)

- Q16** SATURATION SPECTROSCOPY WITH A TUNABLE SIDEBAND LASER  
G. Magerl, W. Schupita (Wien, Austria) ; J.M. Frye, T. Oka (Chicago, U.S.A) ;  
W.A. Kreiner (Ulm, B.R.D)
- Q17** TWO-PHOTON EXCITATION OF CO ( $A^1\pi$ )  
B. Girard, N. Billy, J. Vigué (Paris, France)
- Q18** THE EXCITATION SPECTROSCOPY OF CLUSTERS AND MOLECULES WITH AN INFRARED LASER  
J. Geraedts, G. Luijks, W. Knippers, M. Snels, S. Stolte, J. Reuss (Nijmegen,  
The Netherlands)
- Q19** ETUDE DU SPECTRE MICROONDE DU DICHLORODIFLUOROMETHANE  
P. Trannoy, J. Bellet, E. Willemot (Villeneuve d'Ascq, France)
- Q20** VIBRATIONALLY INDUCED QUADRUPOLE COUPLING IN THE  $\nu_3 = 1$  STATE OF  $^{189}\text{OsO}_4$   
F. Scappini, J. Frye, T. Oka (Chicago, U.S.A)
- Q21** SPECTROSCOPIE A HAUTE RESOLUTION D'UN ION DIATOMIQUE SIMPLE ET DE SES  
ISOTOPES  
A. Carrington, R.A. Kennedy, T.P. Softley (Southampton, U.K) ; P.G. Fournier,  
E.G. Richard (Orsay, France)
- Q22** LOCAL MODE CHARACTER IN THE (2000) STRETCHING OVERTONE OF  $\text{GeH}_4$   
A.J. Robiette (Reading, U.K) ; A.S. Pine (Washington D.C, U.S.A) ;  
S.J. Daunt (Knoxville, U.S.A - Montreal, Canada)
- Q23** P.T. IR SPECTRA OF METHYLENAMINE ON A NICOLET 7199 SYSTEM  
C.M. Deeley, M.L. Lelerre, I.M. Mills (Reading, U.K)

*Les auteurs dont les noms sont soulignés seront présents au Colloque.  
The underlined names are those of authors who are expected to attend the meeting.*



**Conférences invitées**

**Invited lectures**



V. Špirko

The J. Heyrovský Institute of Physical Chemistry and  
Electrochemistry, Czechoslovak Academy of Sciences,  
160 00 Prague 6, Czechoslovakia

Because of the intensity and richness of its spectrum, ammonia has always played a substantial role in the development of molecular spectroscopy. It has provided a large number of easily observable lines on which to try new experimental techniques. The spectrum exhibits, however, just abundance of strong anomalies when analysed in terms of the standard term formulas. To be able to understand its structure properly, new model Hamiltonians (closely related to that developed by Hougen, Bunker and Johns for the study of triatomic molecules) have been developed.

The main purpose of our work was to develop simple theoretical models allowing the determination of the pertaining functions (e.g., the potential energy function), to relate this theory to accessible experimental data, and, to provide reasonable predictions for hitherto non-measured spectral characteristics.

In this lecture some of our results are reviewed concerning the potential energy function, the electric dipole moment function, the Zeeman g-tensor function, the quadrupole coupling function, the spin-rotation coupling functions, and, the spin-spin interaction functions.

HIGH RESOLUTION SPECTROSCOPY OF THE STRATOSPHERIC EMISSION  
IN THE SUBMILLIMETER REGION

B. Carli

Istituto di Ricerca sulle onde Elettromagnetiche  
via Panciatichi, 64  
50127 Firenze - Italy

Most molecules, which play a relevant role in the stratospheric chemistry, display a rotational spectrum in the submillimeter region. This property makes submillimeter spectroscopy an interesting tool for the simultaneous monitoring of several stratospheric minor constituents.

Unfortunately in this spectral region the stratospheric spectrum is also characterized by the presence of numerous lines due to the relatively more concentrated ozone. The detection of the minor constituents becomes possible therefore only when the spectral resolution of the measurement is sufficient to fully resolve the ozone spectrum in order to make possible the study of those features that are present in between ozone lines. This objective sets a stringent resolution requirement in a spectroscopic region where until recently a relatively low resolution has been used.

A Fourier Transform spectrometer, which has been specially designed and built for stratospheric measurements, has proved that the recent technological improvements enable to attain in the submillimeter spectral region an unapodized resolution of  $0.0033 \text{ cm}^{-1}$  and that this resolution is suitable for the detection of several stratospheric minor constituents.

The presence of several unexpected features in the high resolution stratospheric spectrum has spurred new laboratory measurements of several molecules with the same instrument at the same resolution.

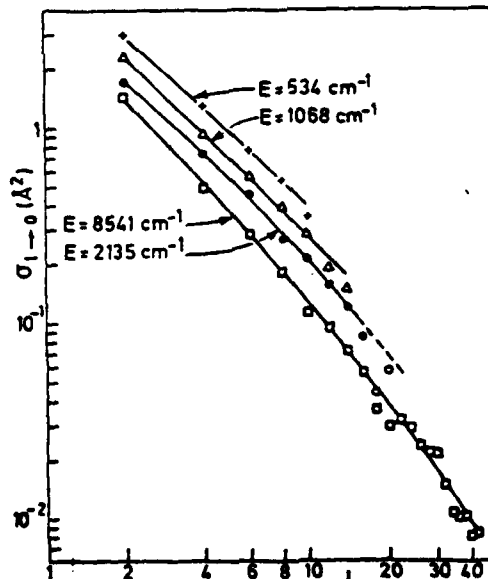
**B**

THE ENERGY DEPENDANCE OF ROTATIONALLY  
INELASTIC CROSS-SECTIONS AND FITTING LAWS

B.J.WHITAKER and Ph.BRECHIGNAC  
Laboratoire de Photophysique Moleculaire  
Universite de Paris-Sud  
91405 Orsay FRANCE

We have investigated the energy dependance of theoretical and experimental data sets for rotational energy transfer in a variety of diatom-atom systems. We find that the data can be well represented by the AON fitting law<sup>1</sup> for the primary set of cross-sections occurring in the IOS factorisation. Assuming that the interaction potential is dominated by a single term of the Legendre polynomial expansion,  $P_\lambda(\cos \Theta)$ , one has:  $\sigma_{j_1 \rightarrow j_2} = c[(a/n)\ln(a/n) - a/n + 1]$ . The two fitting parameters,  $a$  and  $c$ , are explicitly related to the collision energy and to the range and strength of the model potential via a semi-classical description of the collision process. By transforming to two new fitting parameters,  $\alpha = a\sqrt{E_i}$  and  $\gamma = c/\sqrt{E_i}$ , where  $E_i$  is the kinetic energy of the  $i$ th rotational level, we derive the energy dependant form of the AON.

In the figure we show the result of a fit to classical trajectory calculations for  $N_2 + Ar$ <sup>2</sup>. We find that the quantity  $\sqrt{\alpha\gamma}$  which is proportional to the range of the quadrupolar part of the potential, in this example, remains constant while the quantity  $\sqrt{\alpha/\gamma}$  which represents the strength of the potential at the point of closest approach increases with the energy as expected.



This behaviour is equally found for the case of a fit to experimental data for  $HF + Ar$ <sup>3</sup>.

We have also compared partial cross-sections obtained from the AON to quantal calculations of the partial opacities for the  $LiH + He$  system<sup>4</sup>. We find that the AON correctly describes, at least qualitatively, the basic features in particular that small impact parameters are responsible for large  $\Delta j$  changes.

1. B.J.WHITAKER and Ph.BRECHIGNAC Chem.Phys.Lett.(1983)95,405
2. M.D.PATTENGILL and R.B.BERNSTEIN J.C.P.(1976)65,4007
3. J.A.BARNES, M.KEIL, R.E.KUTINA, and J.C.POLANYI J.C.P.(1982)76,913
4. E.F.JENDREK and M.ALEXANDER J.C.P.(1980)72,6452

INVARIANT PARAMETERS OF THE VIBRATION-ROTATION HAMILTONIAN OF TETRA-  
HEDRAL MOLECULES.

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V.G.IYUTEREV, V.I.PEREVALOV

Institute of Atmospheric Optics, TOMSK 634 055 USSR.

J.P.CHAMPION, G.PIERRE

Laboratoire de Spectronomie Moléculaire, ERA 599, Université de DIJON  
6, Bd Gabriel, 21100 DIJON, FRANCE.

=====

The ambiguity of the effective hamiltonians for isolated E and  $F_2$ , interacting E- $F_2$  and  $A_1$ - $F_2$  states is studied. The transformations of these hamiltonians to reduce forms are suggested. The theoretical results are illustrated by numerical analyses on  $^{12}\text{CH}_4$  and  $\text{SiH}_4$ .

EXPERIMENTAL AND THEORETICAL ESTIMATE OF TWO-PHOTON INTENSITIES  
IN THE  $2\nu_2$  BANDS OF  $\text{NH}_3$

A. DI LIETO - Scuola Normale Superiore - Pisa, Italy

P. MINGUZZI, S. PROFETI, M. TONELLI:

Dipartimento di Fisica dell'Università - Pisa, Italy

The development of low pressure optoacoustic (OA) cells has favoured the application of this detection method to high resolution spectroscopy. Since the sensitivity of the cell increases with the incident power, the OA technique appears particularly suited for nonlinear spectroscopy.

In the first part of this work, we present the application of the OA Doppler-free two-photon technique to the study of the  $\text{NH}_3$  infrared spectrum. The experimental apparatus employs two single mode cw  $\text{CO}_2$  lasers to excite transitions in the  $\nu_2 = 0-2$  band. The lasers are operated at fixed frequency on different rovibrational lines and the tuning of the transitions into resonance is obtained by Stark effect. Six different transitions have been observed within the operating range of the cell (up to 36 kV/cm).

Later on, we extended our study to a systematic search of all coincidences between the  $\text{NH}_3$   $\nu_2=0-2$  band and the spectrum of two  $\text{CO}_2$  lasers, obtainable either by a small laser frequency tuning or by a Stark tuning of molecular levels. By assuming a maximum resonant field of 50 kV/cm and a laser tunability of 200 MHz, we theoretically determined more than 70 two-photon transitions with an intensity larger than 1% of those we actually observed. For each of these lines we report the outstanding features, such as the preferred laser lines and the necessary Stark field or laser tuning.

A good agreement is found between theoretical and experimental relative intensities of the observed transitions, except for one line having a nearly resonant intermediate level.

The absolute intensity estimates suggest that further transitions, stronger than those so far detected, should be observable employing the existing apparatus, in particular  $R^2$  transitions, a type never observed before.

In conclusion we report an example of the OA technique sensitivity and we present theoretical results giving useful and reliable indications to extend the two-photon spectrum of  $\text{NH}_3$ .

The  $\nu_1$  bands of  $^{32}\text{S}^{18}\text{O}_2$  and  $^{34}\text{S}^{18}\text{O}_2$  from IR-MW  
double resonance

Josef Lindenmayer, Harold Jones and H.D. Rudolph,  
 Abt. Physikalische Chemie, Universität Ulm,  
 D-7900 Ulm, Bundesrepublik Deutschland

Effective band constants for the  $\nu_1$  bands of both  $^{32}\text{S}^{18}\text{O}_2$  and  $^{34}\text{S}^{18}\text{O}_2$  have been determined from infra-red-microwave double resonance spectroscopy. These results allow conclusions to be drawn over the process involved in previously reported experiments with  $\text{CO}_2$  lasers and oxygen-18 samples of  $\text{SO}_2$ .

The ground state constants were determined from a refit of microwave data from the literature.

	$^{32}\text{S}^{18}\text{O}_2$		$^{34}\text{S}^{18}\text{O}_2$	
	(0,0,0)	(1,0,0)	(0,0,0)	(1,0,0)
A	57.3846(3)	57.4471(3)	55.977(2)	55.6419
B	9.17040(6)	9.12744(6)	9.17085(4)	9.12854
C	7.88950(4)	7.85237(5)	7.85486(3)	7.81867
$\Delta_J \cdot 10^6$	4.7(4)	4.7(6)	5.14(7)	5.14
$\Delta_{JK} \cdot 10^5$	-10.9(8)	-10.4(8)	-9.6(11)	-9.6
$\Delta_K \cdot 10^3$	2.315(26)	2.317(40)	2.147(4)	2.246
$\delta_J \cdot 10^6$	1.26(3)	1.28(5)	1.31(1)	1.31
$\delta_K \cdot 10^5$	1.97(14)	3.2(10)	1.96(10)	1.96
$\nu_1^0$	= 33 012.156(9)		$\nu_1^0$ = 32 780.91(6)	

All values in GHz.



The  $\nu_1$  bands of  $^{32}\text{S}^{18}\text{O}_2$  and  $^{34}\text{S}^{18}\text{O}_2$  from IR-MW  
double resonance

Josef Lindenmayer, Harold Jones and H.D. Rudolph,  
 Abt. Physikalische Chemie, Universität Ulm,  
 D-7900 Ulm, Bundesrepublik Deutschland

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A	57.3846(3)	57.4471(3)	55.977(2)	55.6419
B	9.17040(6)	9.12744(6)	9.17085(4)	9.12854
C	7.88950(4)	7.85237(5)	7.85486(3)	7.81867
$\Delta_J \cdot 10^6$	4.7(4)	4.7(6)	5.14(7)	5.14
$\Delta_{JK} \cdot 10^5$	-10.9(8)	-10.4(8)	-9.6(11)	-9.6
$\Delta_K \cdot 10^3$	2.315(26)	2.317(40)	2.147(4)	2.246
$\delta_J \cdot 10^6$	1.26(3)	1.28(5)	1.31(1)	1.31
$\delta_K \cdot 10^5$	1.97(14)	3.2(10)	1.96(10)	1.96
$\nu_1^0 = 33\,012.156(9)$		$\nu_1^0 = 32\,780.91(6)$		

All values in GHz.

Stark Effect Studies of  $\text{CaCl } X^2\Sigma$   
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In this contribution we report on a novel laser microwave double resonance experiment that was carried out on an effusive molecular beam to observe Stark shifts of rotational transitions in the electronic ground state of  $\text{CaCl}$ .

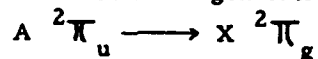
The experimental set-up used consists of an "optical" Rabi molecular beam apparatus in which the "A" and "B" fields are replaced by a single frequency laser beam, depleting and probing the population of a specific ground state rotational level. Microwaves fed into the "C" region by a parallel plate waveguide lead to a repopulation of the depleted rotational level, which in turn causes an increase in fluorescence in the probe region "B". The linewidth of the observed transitions, mainly due to time of flight broadening, is around 20 kHz, allowing the resolution of the hyperfine structure of  $\text{CaCl}$ .

For our Stark effect studies a voltage was applied to the parallel plate waveguide and Stark shifts of several hyperfine components were recorded. The observed shifts have been fitted using a diagonalization treatment of the complete rotational, fine, hyperfine and Stark Hamiltonian in a  $bg_j$  basis set. The fit yielded the following results.

$$\begin{array}{rcl} \text{CaCl } X^2\Sigma & v = 0 & = 4.265(1) \text{ D} \\ & v = 1 & = 4.281(1) \text{ D} \end{array}$$

An additional systematic uncertainty of these values of 0.02 D arises from the limited accuracy in determining the distance between the Stark plates, but this does not affect the accuracy of the difference between the dipole-moments for  $v = 0$  und  $v = 1$ .

Electronic spectra of diatomic halogen cations ( $F_2^+$ ,  $Cl_2^+$ ,  $Br_2^+$ )



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Electronic spectra of the halogen ions have been studied by crossing a rotationally cooled supersonic beam orthogonally with an electron beam; fluorescence from the ions is dispersed in a spectrometer. Electron impact ionisation involves little transfer of rotational angular momentum, so many vibronic states of the ion are produced at a low rotational temperature; the fluorescence spectra are therefore very simple due to the small number of rotational components in each band. This simplification is of paramount importance in the study of the halogen ion spectra.

The spectrum of  $F_2^+$   $A \ ^2\Pi_u \longrightarrow X \ ^2\Pi_g$  is well-behaved. Over 100 vibrational bands have been fitted into two Deslandres tables ( $\nu = 3/2$  and  $1/2$ ), and vibrational constants evaluated. Rotational resolution has also been obtained, and the spectra show a non-Boltzmann (low) temperature distribution. The absolute numbering of the Deslandres tables has been established by comparing observed intensities with those predicted from Franck-Condon calculations: the numbering used by Porter (*J. Chem. Phys.*, 48, 2071) is shown to be incorrect.

The spectrum of  $Br_2^+$  is also well-behaved. Each vibrational band is now a  $1/2/1$  triplet due to isotope splitting (such splittings can only really be seen at a low rotational temperature), but rotational resolution is not obtained. There is a large difference in  $\omega_e$  between the  $A \ ^2\Pi_u \ 3/2$  and  $1/2$  sub-bands due to the closeness of the state to the dissociative limit  $Br \ ^2P_{3/2} + Br^+ \ ^3P_2$ .

The spectrum of  $Cl_2^+$ , however, is severely perturbed. Each band is a  $9/6/1$  isotope triplet, and the Deslandres tables reveal an irregular series of vibrational energy levels in  $A \ ^2\Pi_u$  (also observed by Huberman in 1966, *J. Mol. Spec.*, 20, 29). Rotational resolution has been obtained on some bands, and shows the expected P,R structure of a  $\Pi - \Pi$  transition. States arising from the electron configuration  $\dots(\sigma_g)^2(\pi_u)^4(\pi_g^*)^2(\sigma_u^*)^1$  may be responsible for the extensive vibrational perturbations (Peyerimhoff (Bonn)). It has not yet been possible to correlate this optical emission spectrum of the ion with the highest resolution photoelectron spectrum of the second band of  $Cl_2$  (ionisation to  $A \ ^2\Pi_u$ ) (de Lange (Amsterdam)).

Full details of all three systems will be given at the conference.



A FITTING PROCEDURE FOR  
EXTENSIVELY PERTURBED HAMILTONIANS ;  
APPLICATION TO THE  $A^1\Pi$  STATE OF CO

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A weighted, non linear, least-squares fitting program is carried out for the Hamiltonian of a  $^1\Pi$  state which strongly interacts with numerous perturbing states.

Corrections to the initial set of parameters are computed by using the iterative Marquardt's algorithm. The normal equation matrix and the error vector are calculated from the Hellmann-Feynman theorem, which gives a rapid convergence to the fitting procedure.

Any number of perturbing states :  $^1\Sigma^+$ ,  $^1\Delta$ ,  $^3\Sigma^+$ ,  $^3\Delta$  and  $^3\Pi$  may be simultaneously introduced in the Hamiltonian, whose matrix elements are taken from Bergeman and Cossart (1).

This method is applied to the reduction of the CO  $A^1\Pi$  ( $v=0$ )  $\rightarrow$   $X^1\Sigma^+$  ( $v=0-6$ ) new measurements, recently obtained at Meudon Observatory (2).

It is shown that the best fit of these data, which are extensively perturbed ( $\sim 30\%$  of extra-lines), is obtained with a large Hamiltonian matrix including all the strongly perturbing states.

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THE C  $^2\Pi$  - X  $^2\Sigma^+$  TRANSITION OF BO

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The C  $^2\Pi$  - X  $^2\Sigma^+$  transition of BO has been observed in emission under high resolution in the spectral region from 1700 to 2200 Å. The rotational analysis is given for the first time.

The Zeeman effect in the origin band of the  $\tilde{A}^1A_2 + \tilde{X}^1A_1$   
system of thioformaldehyde.

by

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Singlet-triplet perturbations in the origin band of the  $\tilde{A}^1A_2 + \tilde{X}^1A_1$  system of  $H_2CS$  were originally detected in absorption spectra recorded by Judge and King (1). Clouthier *et al.* (2) have observed magnetic rotation spectra of this band, and were able to draw some conclusions concerning the nature of the perturbing vibronic level of the  $\tilde{a}^3A_2$  state. In the present work, using laser induced fluorescence excitation, Zeeman shifts and splittings have been observed and measured for some of the perturbed lines in this band. Analysis of the data shows that the perturbations arise from the  $F_1$  triplet components, probably through a vibronic-spin-orbit coupling mechanism.

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DIRECT  $\ell$ -DOUBLET TRANSITIONS IN THE  $O1^1O$  STATE OF  
CYANOGEN HALIDES

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Direct  $\ell$ -doublet transitions have been observed for the  $O1^1O$  state of the  $^{127}I^{12}C^{14}N$  and  $^{127}I^{13}C^{14}N$  isotopic species of cyanogen iodide, the  $^{35}Cl^{12}C^{14}N$  and  $^{37}Cl^{12}C^{14}N$  isotopic species of cyanogen chloride and the  $^{79}Br^{12}C^{14}N$  and  $^{81}Br^{12}C^{14}N$  isotopic species of cyanogen bromide in the frequency range 4-22 GHz.

Spectra have been observed at room temperature flowing the samples into the cell using a computer-controlled 33 kHz Stark modulation spectrometer which has been briefly described in (1).

The  $\ell$ -doubling constants ( $q^0$ ,  $q^1$ ,  $q^2$ ) and the asymmetry parameters ( $\eta eQq_z$ ) of the halogen nuclear quadrupole coupling tensors have been derived by using the formula:

$$\bar{V}(F=J \pm M_I) = q^0 J(J+1) + q^1 J^2(J+1)^2 + q^2 J^3(J+1)^3 + \eta eQq_z \bar{Y}(F=J \pm M_I)$$

The constants  $q^1$  have been calculated from the vibrational force fields of Whiffen (2) (3) (4) for the four cyanogen halides using the formulation of Watson (5). Agreement with the observed values is found to be 10% or better and for cyanogen fluoride and cyanogen chloride the isotopic shifts in  $q^1$  are also well predicted.

The origin of the asymmetry of the halogen electric field gradient tensor is primarily a kinematic effect. A simple model due to Javan (6) in which the nuclear quadrupole coupling tensor is constant and has cylindrical symmetry with respect to the carbon-halogen bond accounts for approximately 80% of  $\eta$  for ClCN but only ~65% for BrCN and ICN.

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## MICROWAVE SPECTRUM OF ACETALDEHYDE IN EXCITED TORSIONAL STATES

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The microwave spectrum of acetaldehyde,  $\text{CH}_3\text{CHO}$ , in its ground state has been extensively investigated (1) and tabulated (2) because of its astrophysical interest. However calculations based on these tables fail to account for more than a few isolated lines in the rich but unpatterned spectrum that we have observed over the 10-75GHz range at room temperature. As the lowest vibrational state lies at  $509\text{cm}^{-1}$ , the majority of these unassigned lines must correspond to b-type transitions in excited states of the  $150\text{cm}^{-1}$  torsional motion. By combining Stark effect calculations, double resonance measurements and frequency sum relations, we have been led to assign some forty transitions to the first excited state, which lies approximately halfway up the potential barrier resisting torsion. We have also made measurements of  $J\ 3 \leftarrow 2$  a-type transition frequencies in higher states, and discovered strong rotational resonances in the 2E species.

An analysis of our results in terms of structure relaxation and higher Fourier harmonic contributions to the potential barrier will be presented.

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## MICROWAVE DOUBLE RESONANCE FOURIER TRANSFORM SPECTROSCOPY

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The advantages of pulsed excitation of microwave spectra, especially in conjunction with a supersonically cooled molecular beam, have been illustrated in a recent series of papers originating from several laboratories (1,2,3). We demonstrate that the same techniques when applied to pulsed three-level double resonance lead to a very broadband excitation of the spectrum of the pump transition, which may readily be observed at the probe frequency. Our technique does not rely on recording the time-resolved response to a series of regular pulses, but instead charts the behaviour of the two-photon coherence induced by pump and probe acting together as a function of the time separation of pump pulses. Consequently high-speed digitisation of the probe signal is replaced by precise programmable timing of microwave pulses.

Fourier transform spectra for the  $J(2 + 1)_s - (1 + 0)_p$  systems in OCS and ClCN taken at pump powers up to 6W and pulse spacings as short as 6.67ns are displayed. Although their computed span is limited to 75MHz by the sampling theorem, pump transitions as far from resonance as 120MHz have been observed 'folded' into the resulting spectra. The potential of this work for Doppler-free laser double resonance spectroscopy is outlined.

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THE MOLECULAR STRUCTURE OF AZIDOTRIFLUOROMETHANE,  $\text{CF}_3\text{N}_3$

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The molecular structure of azidotrifluoromethane has been determined by joint analysis of electron diffraction intensities and rotational constants. The following geometric parameters have been obtained: C-F = 1.328 (2), C-N = 1.425 (5) Å,  $N_\alpha=N_\beta = 1.252 (5) \text{ \AA}$ ,  $N_\beta=N_\omega = 1.118 (3) \text{ \AA}$ ,  $\text{CN}_\alpha\text{N}_\beta = 112.4^\circ (0.2)$ ,  $\text{N}_\alpha\text{N}_\beta\text{N}_\omega = 169.6^\circ (3.4)$  and  $\text{FCF} = 108.7^\circ (0.2)$ : The  $\text{CF}_3$  group staggers the azido group and is tilted by  $5.8^\circ (0.4)$  away from the azido group. In the microwave spectrum  $\mu_a$  transitions for  $J = 4 + 5$  and  $5 + 6$  have been assigned for the ground state and several excited states. For excited torsional states transitions up to  $v = 4$  have been observed, showing that the molecule approaches the symmetric rotor limit for high torsional states. For  $v = 4$  the rotational constants B and C become equal.

## THE MICROWAVE SPECTRUM OF PYRROLIDINE

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in collaboration with the groups of Prof. H. Oberhammer (Tübingen, West Germany) and Prof. L.M. Boggia (La Plata, Argentina)

The rotational spectra of the normal and N-D isotopic species of pyrrolidine have been measured. The molecule exists in a bent configuration with the nitrogen atom out of the plane containing the carbon atoms and with the imino hydrogen in the axial position.

The N(14) quadrupole coupling constants have been determined.

The analysis of the rotational spectra of two and three vibrationally excited states for the normal and N-D isotopic species respectively, indicates that both the barriers to pseudorotation and the imino hydrogen inversion are relatively high.

High Resolution Infrared Spectra of Methyleneimine,  
CH<sub>2</sub>NH in the 3 and the 10 $\mu$ m regions

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The short lived species CH<sub>2</sub>NH is of interest both as the simplest imine, and as a molecule found in the interstellar dust clouds (1). In order to facilitate the detection of this species in astronomical sources by infrared spectroscopy, we have extended our previous study of the  $\nu_7$ ,  $\nu_8$  and  $\nu_9$  bands (2,3) to the 3 and the 10 $\mu$ m regions.

CH<sub>2</sub>NH is produced by the pyrolysis of methylamine in a quartz tube at ca. 1000°C, and has a half life of thirty seconds in our system. The high resolution spectra of the 3 $\mu$ m region at an unapodised resolution of 0.01 cm<sup>-1</sup>, and of the 10 $\mu$ m region with an unapodised resolution of 0.006 cm<sup>-1</sup>, were obtained using the Kitt Peak Solar Fourier Transform Spectrometer, and the survey spectra of the 10 $\mu$ m region with a resolution of 0.05 cm<sup>-1</sup> with the Reading University Nicolet FTS, and by degrading the resolution of the high resolution spectra.

The main fundamental vibrations in the 3 $\mu$ m region are the  $\nu_1$ , NH stretching mode, and the  $\nu_2$  and  $\nu_3$ , CH stretching modes. In addition three combination bands are observed. All the bands show evidence of numerous small perturbations. The  $\nu_1$  band at 3262.6 cm<sup>-1</sup> had not previously been observed.

In the 10 $\mu$ m region, some parts have been recorded at sub-Doppler resolution with a laser Stark spectrometer. The spectrum is complex since it consists of transitions to three states,  $\nu_7$ ,  $\nu_8$  and  $\nu_9$ , which are strongly coupled by Coriolis interaction. The  $\nu_8$  state lies ca. 60 cm<sup>-1</sup> above the  $\nu_7$  and  $\nu_9$  states, and hence the effects of Coriolis interaction are less marked. The analysis of the  $\nu_8$  band has been completed and the departures from an "isolated band" can be accounted for by type A and type B Coriolis interactions with the  $\nu_7/\nu_9$  pair. The type A interaction results in a large negative effective  $D_K$  distortion constant, and the type B interaction in large obvious avoided crossings of levels with  $K_a = 4$  and 5 in  $\nu_8$ , with levels with  $K_a = 5$  and 6 in the  $\nu_7/\nu_9$  pair.

Several  $Q_Q$  branches in the  $\nu_7/\nu_9$  region have been assigned using a combination of laser Stark and Fourier Transform spectra. The method analysis of this strongly interacting system is similar to that recently described by Hallin et. al. (4) in the 7.6 $\mu$ m spectrum of di-imide. Model calculations have been performed treating  $\nu_7$ ,  $\nu_8$  and  $\nu_9$  as a strongly coupled three state system.

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High resolution infrared spectra of  $\text{CH}_2\text{Cl}_2$

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Infrared spectra of  $\text{CH}_2\text{Cl}_2$  in the gas have been recorded in the regions 700-1000  $\text{cm}^{-1}$  ( $\nu_3, \nu_9, \nu_7$ ), 1200-1300  $\text{cm}^{-1}$  ( $\nu_8$ ), and 2400-3000  $\text{cm}^{-1}$  ( $\nu_5+\nu_8, 2\nu_8, \nu_2+\nu_8, 2\nu_2, \nu_1, \nu_6$ ), with a resolution of 0.03  $\text{cm}^{-1}$ .

Most of the bands, particularly those assigned to vibrations concerning with the two chlorine atoms, show the presence in natural abundance of  $\text{CH}_2^{35}\text{Cl}^{37}\text{Cl}$  and  $\text{CH}_2^{37}\text{Cl}_2$ .

There seems to be no evidence for  $\nu_6$  ( $\text{CH}_2$  asym. stretch.), observed by Escribano<sup>1</sup> at 3055  $\text{cm}^{-1}$  in the Raman spectra of the gas, and by Palma<sup>2</sup> at 3056  $\text{cm}^{-1}$  in the infrared spectra of the liquid. Even though the resolution is not always sufficient to fully resolve the rotational structure, it still seems possible the analysis of some bands.

Presently an analysis of the  $\nu_2$  band of  $\text{CH}_2\text{Cl}_2$  at about 1269  $\text{cm}^{-1}$ , is being carried out using the ground state constants obtained by Davis<sup>3</sup>. The band, which seems free from interactions and should not be affected by  $\text{CH}_2^{35}\text{Cl}^{37}\text{Cl}$  and  $\text{CH}_2^{37}\text{Cl}_2$  (the isotopic shifts being about zero), has been so far assigned up to  $J = 50$  and  $K = 7$ . Final results will be presented.

The analysis of other bands of  $\text{CH}_2\text{Cl}_2$  and of the corresponding bands of  $^{13}\text{CH}_2\text{Cl}_2$  will be carried out in the near future.

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The Ground State Rotational Spectrum of Ozone ( $O_3$ ) between  $8\text{ cm}^{-1}$  and  $130\text{ cm}^{-1}$ .

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In this work are reported the results of the analysis of the rotational spectrum of ozone between  $8\text{ cm}^{-1}$  and  $130\text{ cm}^{-1}$ , recorded with the I.R.O.E. (Florence) polarizing interferometer (1), with a resolution of  $0.0033\text{ cm}^{-1}$  at  $30\text{ cm}^{-1}$  and  $0.0085\text{ cm}^{-1}$  at  $100\text{ cm}^{-1}$ .

About 1000 transitions with  $J$  up to 58 and  $K_a$  up to 19, measured in the present work, and 170 mm wave transitions previously reported (2) were fitted with the Watson Hamiltonian (3) (both A and S reduction). Sets of rotational and centrifugal distortion constants up to  $P^6$  terms were derived, which reproduce the observed transitions with a standard deviation of about 6 MHz, interferometric measurements, and 0.06 MHz mmwave measurements.

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AIR BROADENED NO LINEWIDTHS IN A TEMPERATURE RANGE  
OF ATMOSPHERIC INTEREST

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Self and N<sub>2</sub>-broadened linewidths of NO in the 5.4 μm band have been measured at 163°K and 295°K using high resolution Fourier Transform Spectroscopy. For each  $\Lambda$  doublet two "apparent" parameters are measured, the observed peak transmission ( $T_{obs}(\sigma_0)$ ) and the half-width at half-height of the observed absorption ( $w$ ). From these parameters, the true value of the half width  $\gamma_{fi}$  is retrieved from a correspondence table, previously built, which gives  $\gamma_{fi}$  as a function of  $T_{obs}(\sigma_0)$ ,  $w$  and  $d$ , distance between the two components of each  $\Lambda$  doublet.

These linewidths have been calculated using the formalism of Robert and Bonamy. The calculated values are in good agreement with the experimental one. Therefore the same formalism can be reasonably used in order to calculate O<sub>2</sub>-broadened widths which cannot be easily measured. Air-broadened linewidths calculations have been performed in the temperature range [163°K-295°K]. From the results the J dependence of the exponent  $m(J)$  which gives the temperature dependence of the widths, according to the power law  $\gamma(T) = \gamma(T_0) (T/T_0)^{-m(J)}$ , has been established.

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CH<sub>2</sub>F<sub>2</sub> : ANALYSE DU SPECTRE IR VERS 9 μm .

IDENTIFICATIONS D'EMISSIONS LASERS LIR

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Le pompage optique de la molécule CH<sub>2</sub>F<sub>2</sub> par le laser CO<sub>2</sub> donne lieu à des émissions laser dans le domaine du lointain IR. L'attribution de ces émissions nécessite l'enregistrement du spectre IR de la molécule à l'aide d'un appareil à haute résolution. Ceci a été fait avec le spectromètre par T.F. de Guy GUELACHVILI. La résolution particulièrement élevée de l'appareil permet de résoudre les transitions rotationnelles et les doublets d'asymétrie pour la plus grande partie de la région étudiée entre 1030 et 1230 cm<sup>-1</sup>.

Les transitions observées sont dues aux deux bandes fondamentales ν<sub>9</sub> et ν<sub>3</sub> centrées respectivement à 1090.126 et 1111.649 cm<sup>-1</sup>. Ces deux niveaux sont fortement couplés par une interaction de Coriolis qui doit obligatoirement être prise en compte. Malgré cette interaction et malgré la densité du spectre le processus d'identification des transitions a pu être mené à bien ce qui a déjà permis d'identifier quelques transitions laser LIR.

RAIE POMPE <sup>12</sup> C <sup>16</sup> O <sub>2</sub> cm <sup>-1</sup>	ABSORPTION IR CH <sub>2</sub> F <sub>2</sub> v J' K' <sub>A</sub> K' <sub>C</sub> - J'' K'' <sub>A</sub> K'' <sub>C</sub>	EMISSION LIR μm	ATTRIBUTION EMISSIONS LIR v J' K' <sub>A</sub> K' <sub>C</sub> - v J'' K'' <sub>A</sub> K'' <sub>C</sub>
9R (44)1092.0075	3 15, 3,13 - 16, 4,12	1448.1	3 15, 3,13 - 3 15, 2,14
		642.6	3 15, 3,13 - 3 14, 2,12
9P (10)1055.6250	9 39, 4,36 - 40, 4,37	657.2	9 39, 4,36 - 9 39, 3,37
		382.6	9 39, 4,36 - 9 38, 3,35
	9 40, 15,25 - 41,15,26	272.3	9 40,15,25 - 9 40,14,26
		158.5	9 40,15,25 - 9 39,14,26

THE INFRARED SPECTRUM OF THE  $2\nu_9^{\pm 2}, \nu_9^{\pm 1} + \nu_{10}^{\pm 1}, 2\nu_{10}^{\pm 2}$  BAND SYSTEM IN ALLENE- $d_4$ .

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The overtone and combination band system due to the  $\nu_9$  and  $\nu_{10}$  rocking and wagging vibrations in allene- $d_4$  has been studied at a resolution of ca.  $0.05 \text{ cm}^{-1}$  from spectra obtained on a Nicolet FTIR spectrometer.

This band system which is of parallel type shows unusual Q-branch structures including band heads due to a strong first order z-type Coriolis resonance between the  $2\nu_9^{\pm 2}, \nu_9^{\pm 1} + \nu_{10}^{\pm 1}, 2\nu_{10}^{\pm 2}$  levels. From ca. 60 assigned Q-branches and ca. 800 assignments of the rotational J-structure we have performed a simultaneous analysis of these levels taking into account the Coriolis interaction between them and vibrational t-type resonances within  $2\nu_9^{\pm 2}$  and  $2\nu_{10}^{\pm 2}$ . Additional (x,y)-Coriolis perturbations occurring in  $2\nu_9^{\pm 2}$  and  $2\nu_{10}^{\pm 2}$  have been identified.

A number of contour simulations of the bands will be presented. From these we derive the following values for the ratio between the unperturbed transition moments:

$$|\rho_1| = \left| \frac{\langle 0 | u_z | 2\nu_9^{\pm 2} \rangle}{\langle 0 | u_z | 2\nu_{10}^{\pm 2} \rangle} \right| = 0.50(5)$$

and

$$|\rho_2| = \left| \frac{\langle 0 | u_z | \nu_9^{\pm 1} + \nu_{10}^{\pm 1} \rangle}{\langle 0 | u_z | 2\nu_{10}^{\pm 2} \rangle} \right| = 0.15(2)$$

It is demonstrated that the sign of  $\rho_1$  and of  $\rho_2 \cdot \zeta_{9a,10b}^{(z)}$  can be determined from contour simulations. We find  $\rho_1 > 0$  and  $\rho_2 \cdot \zeta_{9a,10b}^{(z)} < 0$ .

LINE STRENGTHS ANALYSIS : THE  $\nu_3 - \nu_4$  BAND OF METHANE.

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The absolute strengths of about 600 rotational lines of the  $\nu_3 - \nu_4$  hot band of  $^{12}\text{CH}_4$  have been measured at Jet Propulsion Laboratory from spectral data recorded at 0.011  $\text{cm}^{-1}$  resolution with a Fourier transform spectrometer at Kitt Peak National Observatory. For single, well separated lines, the measurement precision are  $\pm 0.0002 \text{ cm}^{-1}$  for positions and  $\pm 2\%$  for strengths.

First, it has been found that the strengths were badly reproduced (R.M.S.  $\sim 20\%$ ) by the only dominant term (in  $q_3q_4$ ) of the dipole moment independantly of the used formalism : spherical (1) or tetrahedral (2).

Then, the line strengths have been analysed on the basis of the general expansion of the transformed dipole moment operator in  $\text{XY}_4$  molecules (3).

In the case of  $\nu_3 - \nu_4$  - and with the assumption that  $\nu_3$  and  $\nu_4$  are considered and analysed as isolated bands - there are 3 first order terms in the dipole moment ; in the molecular form, they can be written :

$$(1)M(\Gamma) = (R^{1(1,F1)}) \times (a_3^+(F_2) \times a_4^-(F_2))(\Gamma)(F_2) \text{ with } \Gamma = E, F_1, F_2,$$

where  $R^{1(1,F1)}$  is the rotational tensor with  $P_x, P_y, P_z$  components and  $a$  and  $a^+$  are lowering and raising operators for the oscillators.

The corresponding parameters  $(1)_{\mu}(\Gamma)$  have been determined together with the dominant one  $(0)_{\mu}(F_2)$  by a linear fit of 430 single lines. The obtained parameters are :

$$\begin{aligned} (0)_{\mu}(F_2) &= 0.4007 (4) 10^{-1} \text{ (Debye)} \\ (1)_{\mu}(E) &= - 0.963 (50) 10^{-4} \\ (1)_{\mu}(F_1) &= 0.318 (7) 10^{-3} \\ (1)_{\mu}(F_2) &= - 0.338 (6) 10^{-3} \end{aligned}$$

With these parameters, strengths are reproduced with a R.M.S. of 5.6%. The sum of calculated line strengths for all lines with  $J < 14$  is  $0.048 \text{ cm}^{-2} \text{ atm}^{-1}$  (at 296 K).

[1] E.PASCAUD and M.DANG-NHU, J.Mol.Spectrosc. 69, 141-158 (1978).

[2] C.PIERRE, G.PIERRE, J.P.CHAMPION, J.C.FONTANELLA and M.DELPLANQUE, J.Phys. 41, 393-402 (1980).

[3] M.LOETE, Can.J.Phys. (in press).

NEW DERIVATION OF THE POTENTIAL, SPECTROSCOPIC AND MOLECULAR CONSTANTS OF THE  
CARBON DIOXIDE FROM ITS INFRARED SPECTRUM.

\*\*\*\*\*  
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\*\*\*\*\*

The first derivation of the potential energy function of the carbon dioxide molecule from the rotation-vibration spectra of several isotopic species was given in 1979 using an inverse method based upon the algebraized contact transformation formalism (1).

The significant improvement of the quality and of the quantity of the spectroscopic data for various isotopes of CO<sub>2</sub> leads us to carry out a new numerical determination of the potential.

The previous solution, expanded in a power series of quasi normal internal coordinates, was adjusted to the molecular constants  $\nu_0$ , B and D of 315 vibrationnal levels belonging to five isotopic species. With the resulting solution, theoretical values of the spectroscopic and molecular constants were computed for 14 isotopic species for which infrared data are available.

The mean deviations between calculated and experimental constants are :

$33 \times 10^{-3} \text{cm}^{-1}$	for the 255 band centers
$20 \times 10^{-6} \text{cm}^{-1}$	for the 335 inertia constants
$3,4 \times 10^{-9} \text{cm}^{-1}$	for the 355 centrifugal distorsion constants

The comparison of these results with those previously obtained shows a better agreement between theory and experiment when 157 additional molecular constants are included in the data set.

A study of the isotopic behaviour of the spectroscopic constants is in progress.

(1) A. CHEDIN, J. Mol. Spectrosc. 76, 430-491 (1979)

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The Bending Combination States of HCNO

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The infrared spectrum of HCNO was measured in the region 500 - 657  $\text{cm}^{-1}$  with a resolution of 0.006  $\text{cm}^{-1}$ . The bands observed give new data concerning the states  $\nu_5^1$ ,  $2\nu_5^0$  and  $3\nu_5^1$  and in particular the combination states  $\nu_4^1 + \nu_5^1$ ,  $\nu_4^1 + 2\nu_5^0$  and  $\nu_4^1 + 3\nu_5^1$ . The energy levels obtained from the new data and from previous work now define rather completely the various levels of the combination states up through  $\nu_4^1 + 3\nu_5^1$ .

The energy levels were fitted with a semirigid bender model, modified to account for the simultaneous excitation of the quasilinear  $\nu_5$  mode and the degenerate, small-amplitude bending mode  $\nu_4$ . This fit yields an effective bending potential for the quasilinear mode in the first excited state of  $\nu_4$ .

GERMYL FLUORIDE : Simultaneous analysis of  
infrared and millimeter-wave spectra of  
mono-isotopic  $^{74}\text{GeH}_3\text{F}$  and vibration-rotation  
interactions in excited states

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Abstract: Medium-resolution infrared spectra (Nicolet interferometer) and millimeter-wave pure rotational spectra of  $^{74}\text{GeH}_3\text{F}$  in the  $v_n = 1$  ( $n = 2, 3, 5, 6$ ) vibrationally-excited states have been analysed together using a model where the Coriolis coupling between pairs of states ( $n = 2, 5$ ;  $n = 3, 6$ ) is treated explicitly by matrix-diagonalisation and other interactions are included by selective expansion of the matrix before diagonalisation to include up to nine (or exceptionally fifteen) interacting levels. This allows the use of infrared information up to  $J > 50$  without requiring the use of excessively large matrices, while permitting the inclusion of a logically-consistent collection of interaction terms between levels with  $\Delta(k-l) = 0, \pm 3$ .

The  $\nu_6$  band of further isotopic species of  $\text{CF}_2\text{Cl}_2$   
from IR-MW double resonance

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Our IR-MW double resonance study of the  $\nu_6$  band of  $\text{CF}_2^{35}\text{Cl}_2$  (J.Mol.Spectrosc. 91, 87-102 (1982)) has been extended to the isotopic species  $\text{CF}_2^{35}\text{Cl}^{37}\text{Cl}$  and  $\text{CF}_2^{37}\text{Cl}_2$ . Effective band constants for both isotopic species have been determined. The constants of the ground state of  $\text{CF}_2^{37}\text{Cl}_2$  have been determined for the first time. The analysis of the  $\nu_6=1$  state of this species is complicated by what appears to be Coriolis coupling. Automatic assignment programs have been employed to cope with the mass of data accumulated from the double resonance measurements.



ROVIBRATIONAL LEVELS AND TRANSITION MOMENTS INVOLVED IN THE LASER  
EMISSION OF  $^{12}\text{CF}_4$  AT 16  $\mu\text{m}$ .

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The analysis of the combination band  $\nu_2 + \nu_4$  at 10  $\mu\text{m}$ , recorded by A. VALENTIN, has been completed. The results, including two sets of energy parameters, one for the ground state, the second one for the upper state  $\nu_2 = \nu_4 = 1$ , enable us now to predict the energies in both states to  $J = 40$  with an accuracy  $\approx 10^{-3} \text{ cm}^{-1}$ . The individual line strengths have also been derived using the  $\langle \mu_{0,24} \rangle$  value by C.W. PATTERSON and col. (\*).

Then, we have developed a formulation with a view to analyze, in both frequencies and intensities, the hot band  $\nu_2 + \nu_4 - \nu_2$  of which the transitions are involved in the laser emission of  $^{12}\text{CF}_4$  at 16  $\mu\text{m}$ .

Energies and eigenvectors for  $\nu_2 = \nu_4 = 1$  state being calculated from energy parameters above mentioned, the computing program allows now to fit the experimental wavenumbers of the hot band with adjustment of the energy parameters relating to  $\nu_2 = 1$  state.

Picking up as experimental data, the hot transitions observed in the  $\nu_4$  spectrum recorded by J. KAUPPINEN, we have been able to derive a set of energy parameters allowing to predict the energies in  $\nu_2 = 1$  state to  $J = 40$  with an accuracy  $\approx 2 \cdot 10^{-3} \text{ cm}^{-1}$ . So, we could reach these levels with IR accuracy although the  $\nu_2$  band is forbidden. Moreover, absorption line strengths and transition moments have been derived using  $\langle \mu_{2,24} \rangle \approx \langle \mu_{0,4} \rangle$  value by C.W. PATTERSON and col. (\*).

Lastly, all the possibilities of laser emission by  $^{12}\text{CF}_4$  at 16  $\mu\text{m}$ , have been investigated within  $\pm 0.050 \text{ cm}^{-1}$  around the pumping  $\text{CO}_2$  laser lines.

(\* ) C.W. PATTERSON, R.S. McDOWELL, B.J. KROHN, N.G. NERESSON, S.P.I.E., 288  
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ANALYSIS OF  $^{12}\text{C}_2\text{H}_4$  AND  $^{12,13}\text{CCH}_4$  HOT BANDS IN THE  $10\mu\text{m}$  REGION

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Fourier Transform spectra of heated ( $230^\circ\text{C}$ )  $^{12}\text{C}_2\text{H}_4$  and  $^{12,13}\text{CCH}_4$  ethylenes have been recorded from  $840$  to  $1040\text{ cm}^{-1}$  using the F.T. Spectrometer of the Laboratoire de Spectronomie Moléculaire with an apparatus function of  $4 \times 10^{-3}\text{ cm}^{-1}$  (F.W.H.M.) and an absolute precision of  $2 \times 10^{-4}\text{ cm}^{-1}$ .

The quality of the spectra yields to the first observation of the three most intense hot bands of both isotopes. These hot bands,  $\nu_7+\nu_{10}-\nu_{10}$ ,  $\nu_7+\nu_8-\nu_8$  and  $2\nu_7-\nu_7$ , are involved in the pumping processes of ethylene with  $\text{CO}_2$  and  $\text{N}_2\text{O}$  lasers.

For  $^{12}\text{C}_2\text{H}_4$ , the analysis of the  $\nu_7+\nu_8$  band on the basis of F.T. Spectra<sup>\*\*</sup> combined with the observation of the  $\nu_7+\nu_8-\nu_8$  band leads to the full determination and the analysis of the isolated Raman active  $\nu_8$  level with an accuracy better than  $0.001\text{ cm}^{-1}$ . The study of  $\nu_7+\nu_{10}$  and  $2\nu_7$  is more complicated because they are strongly coupled with four other levels.

For  $^{12,13}\text{CCH}_4$ ,  $\nu_8$  is also infrared active so that the hot band  $\nu_7+\nu_8-\nu_8$  has immediately been assigned. The upper states of the observed hot bands ( $\nu_7+\nu_8$ ,  $2\nu_7$ ,  $\nu_7+\nu_{10}$ ) are involved in a 14 levels polyad.

A global analysis treating simultaneously 6 levels for  $^{12}\text{C}_2\text{H}_4$  and 14 levels for  $^{12,13}\text{CCH}_4$  has been undertaken and the results will be discussed.

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<sup>\*\*</sup> Ch. Lambeau, M. De Vleeschouwer, A. Fayt and G. Guelachvili :  
to be published.

## LES INTENSITES DANS LES BANDES

$\nu_5$  et  $\nu_8$  DE L'ALLENE  $^{12}\text{C}_3\text{H}_4$

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Le spectre d'absorption en infrarouge entre 2965 et 3115  $\text{cm}^{-1}$  de  $\text{C}_3\text{H}_4$  a été publié dans l'Atlas de Pine (1). On y trouve principalement pour  $^{12}\text{C}_3\text{H}_4$  les bandes  $\nu_5$ ,  $\nu_8$  (et aussi des bandes chaudes issues de l'état  $\nu_{11} = 1$ ). Une analyse préliminaire de ce spectre nous a permis de retenir, dans le présent travail, des raies non perturbées dont les intensités mesurées ont finalement servi à déterminer séparément des paramètres d'intensité pour chacune des fondamentales étudiées. C'est ainsi que nous avons pu utiliser, pour la bande  $\nu_5$ , 263 raies non perturbées appartenant aux sous-bandes correspondant à  $K'' = 0, 1, 2$  et pour la bande  $\nu_8$ , qui est relativement plus faible, 26 raies dont la plupart se rapportent à  $K'' = 0$ .

Les résultats obtenus sont satisfaisants, en particulier pour la bande  $\nu_5$  dont l'ensemble des raies étudiées peut être reproduit à mieux de 1 %.

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(1) A.S. PINE, Rapport n° NSF/ASRA/DAR 78-24562, 1980.

LES INTENSITES DANS LES BANDES

$\nu_5$ ,  $\nu_7$  et  $\nu_8 + \nu_{11}$  DE L'ETHANE  $^{12}\text{C}_2\text{H}_6$

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Le spectre de l'éthane, enregistré dans la région de la vibration de valence C-H à l'aide d'un spectromètre à différence de fréquences accordable dans l'infrarouge, a été récemment publié par Pine et Lafferty (1), ainsi qu'une liste des nombres d'ondes et des intensités mesurées. On y trouve également des raies identifiées et des valeurs précises des constantes rotationnelles déterminées, à partir des différences de combinaisons pour l'état de base.

Pour compléter cette étude nous nous sommes proposés ici d'étudier les intensités des raies individuelles de vibration-torsion-rotation. Les conditions expérimentales (1) sont favorables à cette étude car les profils observés sont dus presque exclusivement à l'effet Doppler, la largeur de la fonction d'appareil n'étant que de 10 MHz.

Les bandes étudiées sont les suivantes :  $\nu_5$ ,  $\nu_7$  et  $(\nu_8 + \nu_{11})$ . Certaines sous-bandes de ces bandes sont impliquées dans des résonances plus ou moins fortes (1). Nous avons toutefois pu choisir des doublets de torsion non perturbés pour l'ajustage des paramètres d'intensité. Ces doublets sont facilement reconnaissables par l'alternance de leurs intensités dont le rapport est donné théoriquement par celui de leurs poids statistiques nucléaires respectifs.

Nous présenterons les résultats de l'analyse qui, pour chacune des quatre bandes précitées, permettent de reproduire les mesures expérimentales utilisées à mieux de 2 %.

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87, pp. 237-256 (1982).

THE MICROWAVE SPECTRUM OF CYANOFORMAMIDE,  $\text{NCCONH}_2$ .

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Most of the reports in the literature concerning cyanoformamide deal with the preparation of the substance from water and ethanedinitrile,  $\text{C}_2\text{N}_2$ , or water, hydrogen cyanide and oxygen. It is possible to purify industrial waste gases in a catalytic process giving cyanoformamide and oxamide,  $(\text{CONH}_2)_2$ . As catalyst is used e.g. dichromate(2-),  $\text{Cr}_2\text{O}_7^{2-}$ , or copper nitrate,  $\text{Cu}(\text{NO}_3)_2$ .

It is likely that molecular clouds containing water and ethanedinitrile also contain some cyanoformamide, synthesized with salt grains as catalyst. The molecule should therefore be of astrophysical interest.

The rotational constants based on more than 50  $\mu_a$  and  $\mu_b$  lines in the region 18-26.6 GHz will be reported.

THE MICROWAVE SPECTRUM AND STRUCTURE OF CHLOROKETENE

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Microwave spectra have been measured and analysed for four isotopic species of the transient molecule chloroketene,  $\text{C}^2\text{HCCO}$ . Only  $\bar{b}$ -type transitions have been observed. The spectra have been analysed for rotational, centrifugal distortion and chlorine nuclear quadrupole coupling constants. Because of rotational near degeneracies, several perturbations of the hyperfine structure have been found, with the result that the complete quadrupole tensor has been evaluated. An  $r_0$  structure has been determined, and is correlated with the quadrupole coupling constants.

MILLIMETER WAVE SPECTROSCOPY OF UNSTABLE SPECIES

- $\Lambda$  DOUBLING SPECTRUM OF THE CH FREE RADICAL
- ISOTOPIC SUBSTITUTIONS OF  $\text{CO}^+$  IN EXCITED VIBRATIONAL STATES

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The transient species are created and observed in a liquid nitrogen cooled discharge, excited by an RF oscillator operating at 50 MHz and delivering a maximum power of 1000 W.

New results on two very reactive species are presented.

★ Ten lines between  $\Lambda$  doubling levels of the CH free radical have been measured in the 40 - 80 GHz frequency range. The fitting of these data leads to an accurate determination of the CH molecular constants. An unambiguous scheme of hyperfine levels is derived, together with the spontaneous emission coefficients, which are of importance in some astrophysical processes.

★ Transitions of various isotopic species of  $\text{CO}^+$  in different vibrational states ( $v \leq 4$ ) have been observed in the 100 - 230 GHz frequency range. A set of molecular parameters is derived. Particularly the vibrational dependence of the  $^{13}\text{C}$  hyperfine structure is taken into account and the  $\Delta_{01}^{\text{C}}$  and  $\Delta_{01}^{\text{O}}$  mass scaling coefficients, which describe the breakdown of the Born-Oppenheimer approximation are significantly determined.

Millimetre Wave Spectrum of the  $C_{4v}$  Molecule Iodine Oxygen Pentafluoride ( $IOF_5$ )

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The original microwave measurements of Pierce and Cornwell (1) on  $IOF_5$  up to 22 GHz have now been extended to 76 GHz (J17 ← 16). The following ground state parameters have been obtained

$$B_0 = 2131.101(1) \text{ MHz} \quad \text{eq } Q = 553.0(2) \text{ MHz}$$
$$D_J = 143(3) \text{ kHz} \quad D_{JK} = 101(5) \text{ kHz}$$

(Ref. 1:  $B_0 = 2131.090(10)$ ,  $\text{eq } Q = 552.9(6)$ )

$$D_J \text{ --- } , \quad D_{JK} \text{ --- } , \quad \mu = 1.08(10) \text{ D}$$

In addition, we observe the effect of the K-doubling of  $|K| = 2$  transition present in  $C_{4v}$  symmetry (2) corresponding to  $|R_6| \sim 20$  Hz approximately.

An extensive set of excited state lines have also been observed, almost certainly for the state  $v_{11}(E) = 1$  ( $v_{11} = 205 \text{ cm}^{-1}$ ). This spectrum should exhibit the additional  $\ell$ -doubling of  $k\ell = -1$  transitions ( $q_t^-$ ) (3, 4). Preliminary analysis indicates strong  $\ell$ -resonance perturbations and since  $IOF_5$  is almost a spherical top ( $B \sim 2130$  MHz,  $C \sim 2055$  MHz), then the (2,2)  $q_t^+$  interaction denominator ( $C_t - B_t - C_t z_t^2$ ) and the (2,-2)  $q_t^-$  denominator ( $C_t - B_t + C_t z_t^2$ ) are both of magnitude  $\sim |C_t z_t^2|$  and will produce simultaneous  $q^+$  and  $q^-$  resonance perturbations.

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Microwave spectrum of nitrosomethane with asymmetric  $\text{CH}_2\text{D}$  and  $\text{CHD}_2$   
internal rotors

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The microwave spectra of asym- $\text{CH}_2\text{DNO}$  and asym- $\text{CHD}_2\text{NO}$  have been studied in the range 8-42 GHz. Tunnelling within the methyl group between the two equivalent conformations causes splitting of the torsional ground state into a symmetric level ( $0_+$ ) and antisymmetric level ( $0_-$ ). The rotational spectra based on these torsional substates are perturbed by coupling between internal and overall rotation, causing deviations from asymmetric rotor behaviour and the appearance of intersystem ( $0_+ \leftrightarrow 0_-$ ) transitions. Some of the  $J = 1 \rightarrow 2$  transitions in asym- $\text{CH}_2\text{DNO}$  show anomalous nitrogen quadrupole coupling patterns. These observations are accounted for by an accidental degeneracy of the two  $J = 1$  states ( $1_{10}^+$  and  $1_{11}^-$ ) which are coupled by the tunnel effect. Analysis of the quadrupole coupling patterns gives a direct determination of the internal rotation splitting. The quadrupole splittings in asym- $\text{CHD}_2\text{NO}$  are well behaved. A full analysis of the spectra has been achieved using a coupled level Hamiltonian augmented by centrifugal distortion. The pure torsional splittings of asym- $\text{CH}_2\text{DNO}$  and asym- $\text{CHD}_2\text{NO}$  were determined to be 922.4(1) and 162.4(8) MHz respectively.

Certain transitions in the asym-species show deviation from the above treatment as a result of further perturbations caused by accidental degeneracy with  $0_0$  levels corresponding to the symmetrical conformer at infinite barrier. Analysis of the sym-asym coupling has allowed conformational zero-point energy differences to be determined for the partially deuterated nitrosomethanes.

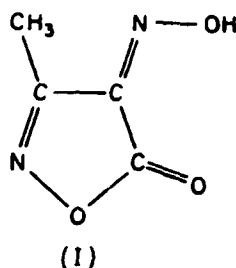
THE ELECTRONIC ABSORPTION SPECTRUM OF THE CNO FREE RADICAL IN THE GAS PHASE

D.A. Ramsay<sup>a</sup> and M. Winnewisser<sup>b</sup>

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W. Germany

An absorption spectrum of the CNO free radical has recently been found  
(1) in experiments on the flash photolysis of 3-methyl-4-oximinoisoxazol-  
5(4H)-one (I).



It was hoped that these experiments might produce a spectrum of the CNOH species. Instead, several well-known band systems were observed in absorption, including those of  $\text{NH}(\bar{A}^3\Pi - \bar{X}^3\Sigma^- \text{ and } c^1\Pi - a^1\Delta)$ ,  $\text{OH}(\bar{A}^2\Sigma^+ - \bar{X}^2\Pi)$ ,  $\text{CN}(\bar{A}^2\Pi - \bar{X}^2\Sigma^+ \text{ and } \bar{B}^2\Sigma^+ - \bar{X}^2\Sigma^+)$ ,  $\text{NCN}(\bar{A}^3\Pi_u - \bar{X}^3\Sigma_g^-)$ ,  $\text{NCO}(\bar{A}^2\Sigma^+ - \bar{X}^2\Pi \text{ and } \bar{B}^2\Pi - \bar{X}^2\Pi)$  and  $\text{HNCO}(\bar{A}^2A' - \bar{X}^2A'')$ . In addition, some violet-degraded absorption features were observed with band heads at 7963.3 Å and 7893.1 Å. These features lie close to the strongest absorption band obtained by the photolysis of fulminic acid,  $\text{HCNO}$ , in a neon matrix (2). The assignment of the matrix bands to CNO was supported by the absence of isotope shifts when DCNO was used and by the rapid isomerisation of the species to NCO on exposure to infrared radiation ( $>7000$  Å). Rotational analysis of the gas phase spectrum shows that it can be assigned to the  $\bar{A}^2\Sigma^+ - \bar{X}^2\Pi$  transition of the CNO free radical, with rotational constants and spin-orbit coupling constant similar to those for the NCO free radical.

(1) D.A. Ramsay and M. Winnewisser, *Chem. Phys. Letters*; in press.

(2) V.E. Bondybey, J.H. English, C.W. Mathews, and R.J. Contolini, *Chem. Phys. Letters* **82**, 208 (1981).

## DIPOLE MOMENT OF THE FO MOLECULE

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National Research Council of Canada,  
Ottawa, Ontario K1A 0R6, Canada.

It has long been a puzzle as to why the FO radical could not be detected by means of gas phase electron resonance spectroscopy or microwave spectroscopy even after extensive study of the closely related group VI-VII diatomics (ClO, BrO, SF, SeF, etc.) with  $2\Pi$  ground electronic states. The recent observation\* of a strong vibrational spectrum of FO using laser magnetic resonance demonstrated that the production of the radical in the gas phase was not especially difficult, and suggested that a small value for the permanent dipole moment might be responsible for the absence of EPR detection.

By applying a moderate (1.4 kV/cm) electric field while observing saturated absorption dips in the LMR spectrum, it has now been possible to measure the dipole moment. The values obtained are amazingly small, and they show a (relatively) large vibrational dependence:  $\mu = 0.0043(4)$  Debye for  $v = 0$ , and  $0.0267(9)$  Debye for  $v = 1$ . This result fully explains why the EPR and microwave spectra of FO have been unobservable.

\*A.R.W. MCKELLAR, Can. J. Phys. 57, 2106 (1979).

FOURIER SPECTROMETRY OF THE LASER INDUCED INFRARED FLUORESCENCE OF  $\text{Cs}_2$

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Fluorescence induced by several exciting lines from an  $\text{Ar}^+$  laser has been recorded by high resolution Fourier Transform spectrometry in the  $4000 - 9000 \text{ cm}^{-1}$  spectral range. Triplet and doublet series are observed and resolved.

The triplet series are due to the fluorescence between a pumped  $^1\Sigma_u^+$  state and a predicted  $^1\Pi_g$  state of gerade symmetry (1). Some 25 series are identified as having this  $^1\Pi_g$  as lower state. Rotational relaxations  $\Delta J = 2, 4$  were observed for the stronger series.

Rotational relaxations in the doublet series confirm that fluorescence is originating from the same upper level as for the triplet series. Preliminary molecular parameters have been obtained for these two firstly observed gerade states of  $\text{Cs}_2$  (2).

(1) G.H. JEUNG, F. SPIEGELMANN, J.P. DAUDEY and J.P. MALRIEU  
J. Phys. B (in press).

(2) C. AMIOT, C. CREPIN, J. VERGES  
Chem. Phys. Lett. (to appear).

MESURE DE LA BANDE  $b^1\Sigma_g^+$  ( $v' = 2$ )  $X^3\Sigma_g^-$  ( $v'' = 0$ ) de  $O_2$  PAR ABSORPTION INTRACAVITE.

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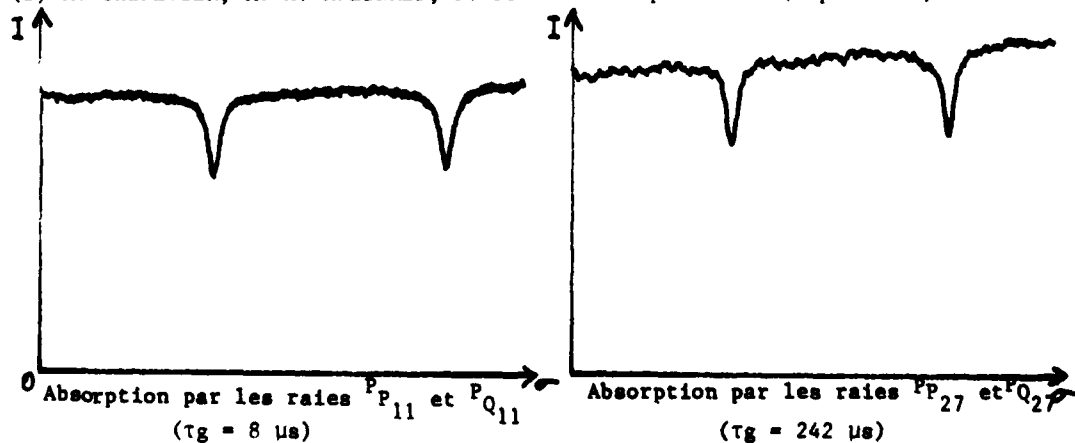
L'absorption intracavité en bande large est une méthode puissante pour détecter des absorptions très faibles. Cette méthode devient quantitative lorsque la technique de la résolution en temps des spectres est mise en oeuvre <sup>(1)(2)</sup>. Ceci consiste à maîtriser le temps de génération,  $\tau_g$ , durant lequel le colorant est pompé, temps durant lequel le spectre à large bande est généré ; le trajet du faisceau dans la cavité est alors équivalent à  $l = c\tau_g$ . Le gaz absorbant, présent dans la cavité perturbe ce spectre, selon la loi d'absorption de Beer-Lambert <sup>(2)</sup>.

Les expériences présentées ici sont réalisées dans le domaine du visible,  $\tau_g$  variant de 10 à 250  $\mu s$  (et donc  $l$  de 3 à 75 km). Elles sont relatives à la transition interdite de  $O_2$   $b^1\Sigma_g^+$  ( $v' = 2$ )  $X^3\Sigma_g^-$  ( $v'' = 0$ ) où les forces de raies,  $k_O^N$  ont été mesurées allant de  $1,7 \cdot 10^{-26}$  à  $5 \cdot 10^{-28} \text{ cm}^{-1} (\text{mol cm}^{-2})^{-1}$ , le gaz  $O_2$  étant dans une cellule sous une pression de 636 Torr.

Ces mesures n'ont pu être réalisées que grâce à une méthode de dépouillement par fit permettant de déterminer simultanément la force de raie et la largeur collisionnelle connaissant la largeur doppler et la fonction d'appareil. C'est la première fois que les forces de raies relatives à cette bande sont mesurées sans extrapolation de valeurs relatives à la bande supérieure.

(1) F. STOECKEL, M. A. MELIERES, M. CHENEVIER ; J. Chem. Phys. 76 (1982) 2191

(2) M. CHENEVIER, M. A. MELIERES, F. STOECKEL . Optic Com. (à paraître).



STUDY OF THE PREDISSOCIATION OF THE  $\tilde{A}^2\Sigma^+$  STATE OF  $N_2O^+$   
USING HIGH RESOLUTION LASER SPECTROSCOPY

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Canada, N6A 3K7.

Using an electrostatic energy analyzer together with a fast-ion-beam laser spectrometer, we have measured the kinetic energy spectrum of  $NO^+$  photofragments produced in the slow predissociation of  $N_2O^+$  prepared in specific vibrational and rotational levels of the  $\tilde{A}$  excited electronic state<sup>(1)</sup>.

The observed energy spectrum shows :

- a narrow distribution of the total kinetic energy for each of the studied vibrational levels of the  $\tilde{A}^2\Sigma^+$  state (100, 110 and 020)
- an absence of structure which must be assigned to a large redistribution of rotational energy.

From the analysis of various energy spectra which corresponds to total released kinetic energy of about 1 eV, we come to the conclusion that a large fraction of the  $NO^+$  photofragments are produced in the  $v = 4$  vibrational level of the  $X^1\Sigma$  state.

Reference :

- (1) J. LERMÉ, S. ABED, R. A. HOLT, M. LARZILLIERE, and M. CARRÉ,  
Chem. Phys. Letters, 96 (1983) 403.

## LASER PREDISSOCIATION SPECTRA OF $\text{PH}_2^+$

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Department of Chemistry  
University of Nottingham  
University Park  
Nottingham, U.K. NG7 2RD

The first electronic spectrum of the  $\text{PH}_2^+$  molecular ion has been recorded in a laser/ion beam experiment. Spectra are recorded by detection of fragment ions which arise from predissociation of an excited electronic state. Predissociation spectra have been observed in two dissociative channels,  $\text{PH}_2^+ \rightarrow \text{P}^+ + \text{H}_2$  and  $\text{PH}_2^+ \rightarrow \text{PH}^+ + \text{H}$ .

A spectrum at  $1 \text{ cm}^{-1}$  resolution has been obtained between 420 n.m. and 670 n.m. by detection of the  $\text{P}^+$  ion. By analogy with the known absorption spectrum of  $\text{SiH}_2$  we expect the  $\tilde{\text{A}}^1\text{B}_1 + \tilde{\text{X}}^1\text{A}_1$  spectrum to fall in this region, and we tentatively attribute at least some of the lines of our spectrum to this transition in  $\text{PH}_2^+$ . A characteristic separation between bands of approximately  $1200 \text{ cm}^{-1}$  is found and is in good agreement with the expected ground state bending vibrational frequency. The rotational structure is unusual. Each vibrational band consists of a few series of very strong lines with typically six members in a series and each line separated by about  $160 \text{ cm}^{-1}$ , overlapped by many weaker lines. The origin of these strong lines is not yet known.

A second spectrum of  $\text{PH}_2^+$  is obtained by detection of the  $\text{PH}^+$  fragment ion between 590 n.m. and 640 n.m. It consists of 5 vibrational bands with a relatively simple rotational structure which we attribute to the  $\tilde{\text{B}}^1\text{A}_1 + \tilde{\text{A}}^1\text{B}_1$  transition in the ion.

Doppler-free two photon infrared spectroscopy with  
a Fabry-Perot resonator.

F. Herlemont, M. Azizi and J. Lemaire

Laboratoire de Spectroscopie Hertzienne associé au CNRS

n° 249 Université de Lille I

59655 Villeneuve d'Ascq Cedex France

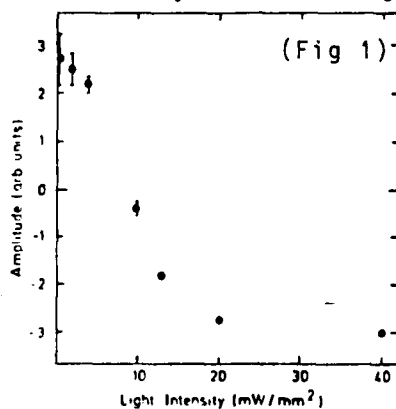
Infrared spectroscopy has been performed using a  $\text{Co}_2$  laser and a Fabry-Perot resonator filled with  $\text{SF}_6$  as saturable absorber. Transmitted as well as reflected power displays sharp Doppler-free two-photon (DFTP) transitions of the  $0. 2\nu_3$   $\text{SF}_6$  band. The DFTP dispersion can be easily observed with the experimental set-up



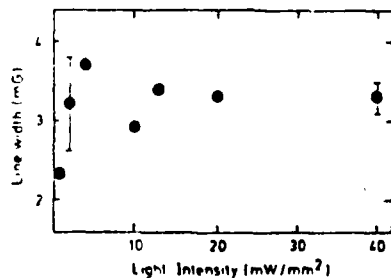
## RADIATIONLESS TRANSITIONS IN MOLECULES STUDIED BY LASER SATURATION EFFECTS

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Physikalisches Institut, Universität Heidelberg, Philosophen-  
weg 12, D-6900 Heidelberg, West Germany

We report on experiments which indicate that the excited state  $|a\rangle$  of an isolated molecule prepared by light absorption is different from the radiatively decaying state  $|b\rangle$  of this molecule. Obviously the isolated molecule performs a radiationless transition from  $|a\rangle$  to  $|b\rangle$ . In the experiments a beam of  $\text{NO}_2$  molecules is irradiated by a cw single mode dye laser. The measured quantity is the degree of polarization of the laser induced molecular fluorescence versus external magnetic fields. That means for instance Hanle effect and double resonance experiments. Generally we find that the signal amplitudes depend nonlinearly on the light intensity of the exciting laser light. On some molecular absorption lines the nonlinearity is so strong that the signal amplitudes even



(Fig 1) change the sign as shown for instance in Fig 1. This figure depicts the "normalized" signal amplitude of a Hanle signal, i.e. the signal amplitude divided by the total fluorescence intensity. Fig 2 shows that the width of this signal is however independent on the light intensity. These and similar results are explained assuming a radiationless transition between the states  $|a\rangle$  and  $|b\rangle$ .



(Fig 2)

DAY-TIME VARIATION OF ATMOSPHERIC NO<sub>2</sub>  
FROM HIGH RESOLUTION FOURIER TRANSFORM SPECTRA

J.-M. Flaud and C. Camy-Peyret

Laboratoire de Physique Moléculaire et d'Optique Atmosphérique  
Bât. 221, Campus d'Orsay, 91405 Orsay Cedex, France

D. Cariolle

E.E.R.M, Centre National de la Recherche Météorologique  
31057 Toulouse Cedex, France

J. Laurent

O.N.E.R.A, 92320 Châtillon s/Bagneux, France

and G.M. Stokes

Batelle, Pacific Northwest Laboratories  
P.O.Box 999, Richland, Washington, U.S.A, 99352

Using the sun as a source, several high resolution ( $\delta\sigma = 7 \times 10^{-3} \text{ cm}^{-1}$ ) atmospheric Fourier transform spectra have been recorded at the Kitt Peak National Observatory during the same day. Using the improved spectroscopic data (line positions and intensities) generated in our group [Perrin et al., 1982], it has been possible, for the first time, to recognize unambiguously several NO<sub>2</sub> absorption peaks in the relatively clear atmospheric window located around 3.5  $\mu\text{m}$ . Hence the possibility to measure reliably NO<sub>2</sub> column densities from the ground has been established [Camy-Peyret et al., 1983]. Indeed, up to now, the only available infrared results concerning atmospheric NO<sub>2</sub> concentrations were obtained from air-borne measurements in the 6.2  $\mu\text{m}$  region which is not suitable for NO<sub>2</sub> detection from the ground because of the very strong absorption of the  $\nu_2$  band of water vapor. A total of 16 spectra have been recorded on September 20, 1982, allowing a precise determination of the variation of the NO<sub>2</sub> column density during the day. From sunrise to noon, one observes a rapid increase of the amount of NO<sub>2</sub>, followed by a slower increase of this amount from noon to sunset.

Although the observed values of the vertical column densities are lower than those calculated by the photochemical model developed at EERM, their variation during the day are particularly well reproduced by this model.

A. Perrin, J.-M. Flaud and C. Camy-Peyret  
Infrared Phys. 22, 343-348 (1982)

C. Camy-Peyret, J.-M. Flaud, J. Laurent and G.M. Stokes  
Geophys. Res. Lett. 10, 35-38 (1983).

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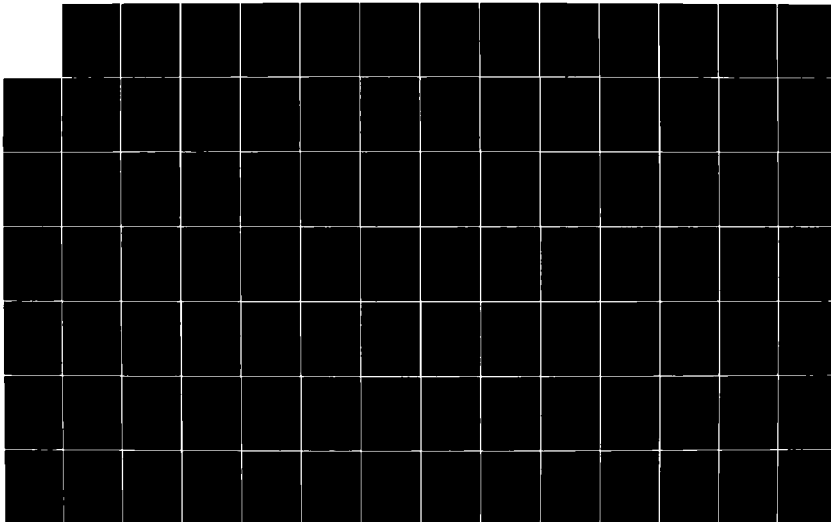
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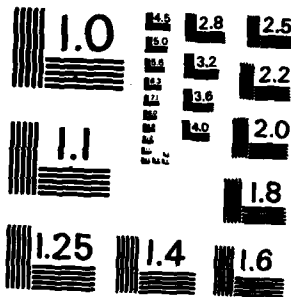
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MICROCOPY RESOLUTION TEST CHART  
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DIPOLE STRENGTH AND ELECTRICAL PROPERTIES OF SMALL MOLECULES

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a CNR, Unità di Spettroscopia in Milano dell'Istituto di Chimica Fisica Applicata dei Materiali di Genova

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c Istituto di Fisica Sperimentale del Politecnico di Milano, piazza L.da Vinci 32.

The experimental infrared intensities and the electrical dipole moments can provide phenomenological parameters (equilibrium charges and charge fluxes, ECCF) which describe the charge distribution on atoms.<sup>(1,2)</sup>

The experimental ECCF help in the understanding of some electrical properties of small molecules<sup>(3)</sup> (size of the atomic charges, high or low deformability of the charge with vibration, tendency of the bonds to dissociate into ions or neutral atoms).

This information, derived directly from experiments, can be used to classify atoms according to their capability of forming hydrogen bonds,<sup>(4)</sup> to estimate the formation energy of weak molecular complexes<sup>(5)</sup> and, in general, to interpret the spectra of larger molecules.<sup>(6)</sup>

1. M.Gussoni "Advances in Infrared and Raman Spectroscopy." (R.J.H.Clark and R.E.Hester, eds.), vol.6, Heyding, London 1980
2. M.Gussoni, P.Jona and G.Zerbi, J.Chem.Phys., in press
3. M.Gussoni, C.Castiglioni and G.Zerbi, J.Phys.Chem., submitted
4. M.Gussoni, C.Castiglioni and G.Zerbi, J.Chem.Phys., submitted
5. M.Gussoni, C.Castiglioni and G.Zerbi, Chem.Phys.Letters, in press;
6. G.Zerbi, M.Gussoni, S.Abbate and P.Jona, in "Vibrational Intensities in Infrared and Raman Spectroscopy" (W.B.Person and G.Zerbi, eds), Elsevier, Amsterdam 1982

DAY-TIME VARIATION OF ATMOSPHERIC NO<sub>2</sub>  
FROM HIGH RESOLUTION FOURIER TRANSFORM SPECTRA

J.-M. Flaud and C. Camy-Peyret

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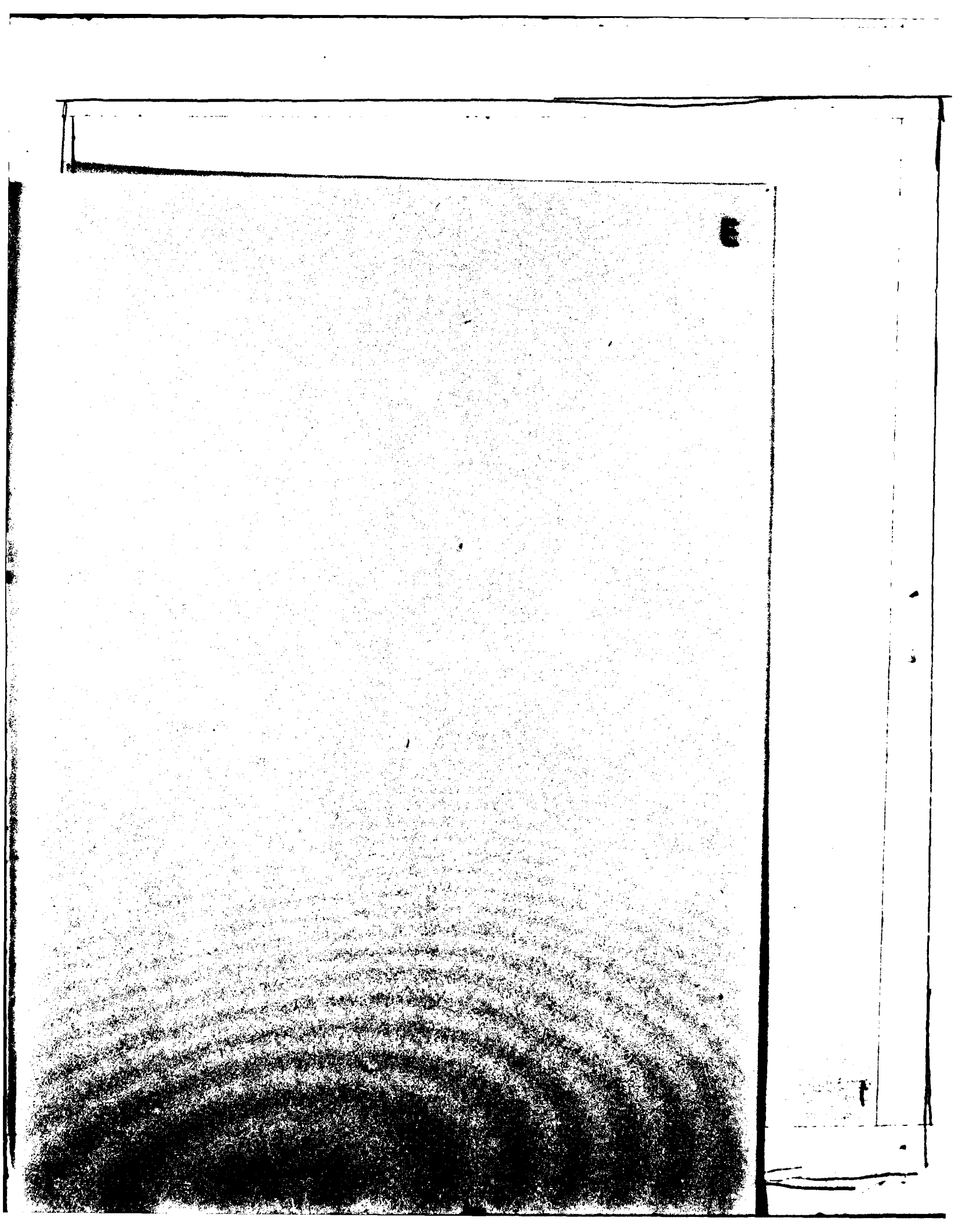
QUASI-SYMMETRIC TOP MOLECULE APPROACH TO THE ROTATIONAL-  
VIBRATIONAL PROBLEM OF  $\text{CH}_3\text{XY}$  MOLECULES

Application to  $\text{CH}_3\text{C}^{15}\text{N}$

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A new approach to the rotational-vibrational problem of molecules of the  $\text{CH}_3\text{XY}$  type is proposed. The approach can be applied equally to both a symmetric top and asymmetric top  $\text{CH}_3\text{XY}$  molecule. The molecule is considered as vibrating, internally rotating about the CX bond of the effectively bent CXY skeleton, and rotating in space. The zeroth-order approximation, in which the CXY bending motion, internal and overall rotations are explicitly taken into account, is discussed. The approach is applied to analyze the rotational spectrum of  $^{15}\text{N}$  methyl cyanide in the ground, first and second excited states of the CCN bending mode.





ON DIFFERENT CRITERIONS OF CONSIDERATION OF  
ANHARMONIC RESONANCES IN TRIATOMIC MOLECULES

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Dnepropetrovsk, USSR

V.F.Golovko

Institute of Atmospheric Optics, Siberian Branch,  
USSR Academy of Sciences, Tomsk, 634055, USSR

ALGEBRAIC MANIPULATIONS WITH VIBRATION-ROTATION IRREDUCIBLE TENSORS.

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Department of Chemistry, Moscow State University, Moscow  
117 234 USSR

The general technique for the manipulation with the irreducible tensor operators for spherical top molecules is proposed. The standard form of the irreducible tensor operators is defined which enables one to make the operator calculations taking into account the operator indexes only. The main technical problem is the explicit calculation of the vibration rotation commutators /anticommutators/

$$\begin{aligned} & [(V^r \cdot R^{\Omega_1(J_1 t_1 r)})^A, (V^{r'} \cdot R^{\Omega_2(J_2 t_2 r')})^A] = \\ & = \frac{1}{2} \sum_x \sqrt{\frac{[x]}{[r][r']}} \left[ \left\{ [V^r, V^{r'}]_-^x \cdot [R^{\Omega_1(J_1 t_1 r)}, R^{\Omega_2(J_2 t_2 r')}]_+^x \right\}^A \right. \\ & \quad \left. + \left\{ [V^r, V^{r'}]_+^x \cdot [R^{\Omega_1(J_1 t_1 r)}, R^{\Omega_2(J_2 t_2 r')}]_-^x \right\}^A \right]. \end{aligned}$$

The rotational part are calculated explicitly by using the  $\langle\langle J_1, J_2 \rangle\rangle \delta, \bar{J}_3 \rangle$  symbols, introduced by author [1].

$$\begin{aligned} [R^{\Omega_1(J_1 t_1 r)}, R^{\Omega_2(J_2 t_2 r')}]_x^x &= \frac{1}{\sqrt{[x]}} \sum_{J_3 t_3} \sum_{\delta} (1 \pm (-1)^{J_1+J_2+J_3}) \\ & (-1)^{J_3} \sqrt{2J_3+1} K_{t_1 r, t_2 r', t_3 x}^{J_1 J_2 J_3} \langle\langle J_1, J_2 \rangle\rangle \delta, \bar{J}_3 \rangle R^{\Omega_1+\Omega_2-\delta(J_3 t_3 x)} \end{aligned}$$

The tensor form of wick theorem is applied for the calculation of the vibrational part. The graphical approach is formulated which facilitate the calculations.

The algebraic treatment is used for the theoretical analysis of the  $XY_4$  experimental data treatments and the calculation of the spectroscopic parameters by the contact transformations.

1. B.I.Zhilinskii, Optika i spektr., 51, 474 (in Russian) (1981)

GENERAL AND EXEMPLIFIED THEORY OF RELAXATION.

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Fysisch Laboratorium, Rijksuniversiteit Utrecht,  
Princetonplein 5, Utrecht, The Netherlands.

Various kinds of experiments have been performed on relaxation lately (see e.g. our second contribution to this colloquium), both steady-state and time-dependent, both in absorption (double-resonance techniques) and in fluorescence (LIF).

Theoretical description is usually given by means of a gain-loss (or *master*) equation for the population of the  $i$ -th level:

$$\frac{dn_i}{dt} = \sum_{j \neq i} P_{j \rightarrow i} \cdot n_j - \sum_{j \neq i} P_{i \rightarrow j} \cdot n_i$$

where  $P_{i \rightarrow j}$  is the probability (per unit of time) for a system in level  $i$  to jump to level  $j$ , either by a binary collision or by absorption or stimulated emission due to an external radiation field (no self-absorption). Constraints on the  $P$  are in general poor, but already under weak assumptions important physical consequences can be derived.

An interesting example is found in the steady-state study of excited electronic state relaxation. Spontaneous decay works as an internal "clock", so collisional lifetimes are measured relative to radiative lifetimes. In this case, from a modified master equation for the fluorescence intensities rather than for the populations and allowing for collisional transitions to (but not from) non-radiating (and therefore undetected) states (*quenching*), it turns out to be possible to derive both collisional and quenching lifetimes from *relative* intensity measurements only. The so derived formulae are exact and apt for further computational processing.

Complications are expected when several lines are not experimentally separated (e.g. because fluorescence is not fully spectrally resolved). The description for such experiments will also be given.

In this contribution we do not intend to explain all mathematical details. Our main interest lies in explaining which physical consequences are valid under which assumptions and elucidating the theory with the aid of a few systems, some of which are being studied at present (e.g. homo- and heteronuclear diatomics).

Infrared-Infrared Double Resonance of CH<sub>2</sub>NOH and CHD<sub>2</sub>F Using an  
Acousto-optically Modulated CO<sub>2</sub> Laser

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Infrared-infrared double resonance, using a cw single mode CO<sub>2</sub> laser and single sideband acoustic-optic modulators of centre frequencies of 50 and 100 MHz, has been used to study CH<sub>2</sub>NOH, CHD<sub>2</sub>F and related light rotors used in optically pumped lasers.

The spectrometer is controlled by means of an Apple II microcomputer, using a combination of equipment linked via an IEEE 488 standard interface bus, and dedicated cards to read the BCD output of the digital voltmeter, and to produce a ramp for Stark field control. The spectra were recorded with either 1 or 0.5 volt step sizes, and stored on floppy discs for subsequent plotting and peak finding.

The observation of the M-resolved components of an asymmetric top double resonance transition in CHD<sub>2</sub>F has given an estimate of the rotational asymmetry splitting of this high J transition. Electric quadrupole structure has been resolved in the double resonance spectra of CD<sub>3</sub>I, SiH<sub>3</sub>Br and CD<sub>3</sub>Br. The study of the CH<sub>2</sub>NOH spectrum is being coupled with the simultaneous analysis of the high resolution Fourier Transform spectrum obtained using the Rutherford-Appleton Laboratory Bomem interferometer.

QUANTUM BEAT SPECTROSCOPY IN THE B  $^1\Sigma^+$  STATE OF MgO

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Using a modified Broida-type oven with Argon as carrier gas and  $N_2O$  as oxidant we have produced MgO molecules in the gas phase. The molecules have been detected by laser induced fluorescence and laser excitation spectroscopy. Furthermore, we will report on Stark quantum beat measurements and the determination of electric dipole moments in the electronically excited B  $^1\Sigma^+$  state.

DIFFERENCE FREQUENCY LASER SPECTROSCOPY OF IONS AND FREE RADICALS

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Among various infrared laser sources, c.w. difference frequency laser is a unique source for high-resolution spectroscopy, because of its wide range of frequency tunability ( $2400\text{-}4400\text{ cm}^{-1}$ ). A high-resolution spectrometer with this laser as a source has been developed by Pine. Oka constructed a similar system, and succeeded in detecting  $\text{H}_3^+$ .

We have observed the vibration-rotation transitions of  $\text{HeH}^+$ ,  $\text{NeH}^+$ ,  $\text{ArH}^+$ ,  $\text{HCO}^+$ ,  $\text{OH}$ ,  $\text{OD}$ ,  $\text{NH}$ ,  $\text{SH}$ ,  $\text{SO}$  ( $\nu=3-0$ ),  $\text{NH}_2$  ( $\nu_1, \nu_2$ ),  $\text{DO}_2$  ( $\nu_1$ ), and  $\text{CH}_3$  ( $\nu_3$ ) with a difference frequency system incorporated with a multipass absorption cell and various modulation techniques such as frequency, Zeeman, and discharge modulations.

Finer details of the instrument and some interesting results will be presented.

NEW RESULTS FOR UTILIZATION OF THE ATLAS OF  $^{130}\text{Te}_2$  RECORDED BY F.T.S.

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For a few years we have been trying to get a good wavelength substandard by using the  $^{130}\text{Te}_2$  absorption spectrum recorded between 16000 and 23700  $\text{cm}^{-1}$  by F.T.S. (about 60.000 lines). This time, we present the values of the molecular constants  $D'$ ,  $H'$ ,  $L'$  for the  $\text{AO}_u^+$  state ( $v' = 0$  to 35) and the localization of all the perturbations for this state ( $v' = 5, 10, 12, 15, 20, 28$ ); as the atlas of  $^{130}\text{Te}_2$  edited by the Aimé Cotton Laboratory contain also lines of  $\text{BO}_u^+ - \text{XO}_g^+$  system, we identified about twenty of its bands, particularly new ones corresponding to  $v' \leq 5$  and we obtained molecular constants for these states. As molecules of the VI-VI group may be used as a basis for a line tunable optically pumped laser, we measured the lifetimes at zero pressure and the quenching cross sections of  $\text{AO}_u^+$  vibrorotational states by laser induced fluorescence on the non-perturbated states  $v' = 16$  and 17.

The emission spectrum of the NCO radical

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The NCO radical was produced by a radio-frequency discharge through flowing  $C_2H_5NCO$ . The strongest bands in the 4300-4700  $\text{\AA}$  region have been photographed in high orders of a 7 m vacuum Ebert spectrograph. They belong to the  $A^2\Sigma^+ - X^2\Pi_1$  electronic transition. In addition to the ground state vibrational levels (0,0,0) and (0,1,0) which are already known from the absorption spectrum<sup>1,2</sup>, we observed higher levels in the bending vibration  $\nu_2$  as well as in the two stretching vibrations  $\nu_1$  and  $\nu_3$ .

We have also obtained a laser induced fluorescence spectrum using a c.w. dye laser and exciting the (0,0,0) level in  $A^2\Sigma^+$ . The observations are in good agreement with previous work<sup>3</sup> carried out with a Nd:Yag pumped dye laser.

<sup>1</sup>R.N. Dixon, Phil. Trans. Roy. Soc. Lond. A 252, 165 (1960).

<sup>2</sup>P.S.H. Bolman, J.M. Brown, A. Carrington, I. Kopp and D.A. Ramsay, Proc. Roy. Soc. Lond. A 343, 17 (1975).

<sup>3</sup>B.J. Sullivan, G.P. Smith and D.R. Crosley, 36th Annual Symposium on Molecular Spectroscopy, Columbus, Ohio (1982).





INFRARED FOURIER SPECTROMETRY OF TWO  $^{14}\text{C}$  CONTAINING COMPOUNDS  
CN AND CO

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A microwave discharge through  $^{14}\text{CO}$  radioactive carbon monoxide lead to the formation of  $^{14}\text{CN}$  and  $^{14}\text{CO}$  infrared spectra. These were recorded through high resolution Fourier Transform spectrometry.

The "red"  $A^2\Pi \rightarrow X^2\Sigma^+$  system of  $^{14}\text{CN}$  was first observed in the laboratory. The wavenumbers of the two bands (0-0) and (0-1) were reduced simultaneously to give molecular parameters for the  $A^2\Pi(v=0)$  and  $X^2\Sigma^+(v=0,1)$  vibrational levels (1).

The infrared emission spectrum of the  $^{14}\text{CO}$   $\Delta v=2$  sequence has been recorded with the same interferometer between  $3000\text{ cm}^{-1}$  and  $4300\text{ cm}^{-1}$ . More than 750 spectral lines have been assigned for a wide range of rotational ( $J=0-60$ ) and vibrational quantum numbers ( $v=0-13$ ). Using a fully quantum mechanical variational method (I.P.A.) lead to the obtention of an accurate potential energy curve. With this potential  $G(v)$  and  $B(v)$  values were calculated in very good agreement with those of the direct determination. Also the centrifugal distorsion constants  $D(v)$ ,  $H(v)$ ,  $L(v)$  were calculated by HUTSON's method (3) ; they agree with the "experimental" values. The I.P.A. potential was compared with the semi-classical R.K.R. one.

- (1) C. AMIOT, J. VERGES  
Chem. Phys. Lett. 95, 189 (1983).
- (2) C. AMIOT, J. VERGES, C.R. VIDAL  
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- (3) J.M. HUTSON  
J. Phys.B. 14, 851 (1981).

SPECTROSCOPIC INVESTIGATIONS ON THE COUPLING OF IONIC AND  
COVALENT STATES OF NaI

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Using frequency-doubled and -mixed laser radiation, rotational fine structure in the electronic transition  $O^+ - X^1\Sigma^+$  of NaI was observed and assigned in the region between 26000 and 34000  $\text{cm}^{-1}$ .

Throughout the whole investigated region fragmentary rotational fine structure is observed indicating intermediate coupling of the ionic and covalent state above the ground state dissociation energy. This is described by the semiclassical model of Child for predissociating states /1/.

The complete assignment and analysis of the observed spectra leads to vibrational quantum numbers and molecular constants of the involved states and thus via RKR calculations to the shape of the  $O^+$  potential well created by the intermediate coupling.

/1/ M. S. Child, Mol. Phys. 32, 1495 (1976)

INFLUENCE OF THE SOURCE FREQUENCY NOISE IN HIGH  
RESOLUTION SPECTROSCOPY

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In high resolution spectroscopy experiments, the used c.w. sources exhibit instabilities, mainly related to frequency fluctuations, which may reduce the actual resolution.

The influence of the source frequency noise has been experimentally considered for the saturated absorption case (Lamb - Dip) as well as for the transient absorption case (photon echoes). In this purpose, the frequency of a nearly perfect source (phase locked 3-mm klystron) is modulated by a well defined noise, allowing a separated adjustment of the amplitude and the rate of frequency fluctuations. Let us emphasize that this is necessary for a complete description of the source frequency noise, since a given spectrum width of the e.m. field may be obtained with very different pairs of these two parameters.

Whereas in saturated absorption, the resolution is always bounded by the spectrum width of the e.m. field (irreversible limit), transient experiments exhibit different behaviours according to the rate of frequency fluctuations : particularly, multiple photon echo experiments, optical analogs of N.M.R. Carr Purcell echoes, are not affected by the source frequency fluctuations when their correlation time is long by comparison with the time delay between nutation pulses (reversible limit). Finally, photon echo experiments reveal as a tool for estimating the very short term Allan variance.

MILLIMETER WAVE SPECTRA OF MOLECULES OF  
ASTROPHYSICAL INTEREST

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The development of a millimeter-wave spectrometer using a superheterodyne detection has been continued in our laboratory (1). It now allows routine measurements between 50 and 320 GHz. With a cooled InSb detector measurements up to 600 GHz may be performed. With this spectrometer the millimeter-wave spectra of molecules of potential interest to radioastronomers have been measured for already several years : OCS (2), CH<sub>3</sub>CN (3), CH<sub>3</sub>COOH (4), CH<sub>3</sub>C≡CH (5), CH<sub>2</sub>(CN)<sub>2</sub> (1), CH<sub>3</sub>CH<sub>2</sub>CN (6), CH<sub>3</sub>C≡CCN (7).

New results concerning molecules with internal rotation will be reported.

- |     |                    |  |
|-----|--------------------|--|
| (1) | J. BURIE et al.    | J. Physique <u>43</u> (1982) 1319            |
| (2) | A. DUBRULLE et al. | Z. Naturforsch. <u>35a</u> (1980) 471        |
| (3) | D. BOUCHER et al.  | J. Phys. Chem. Ref. Data <u>9</u> (1980) 659 |
| (4) | J. DEMAISON et al. | J. Mol. Spectr. <u>94</u> (1982) 211         |
| (5) | A. BAUER et al.    | J. Phys. Chem. Ref. Data <u>8</u> (1979) 537 |
| (6) | J. BURIE et al.    | J. Mol. Spectr. <u>72</u> (1978) 275         |
| (7) | A. MOÏSES et al.   | J. Mol. Spectr. <u>92</u> (1982) 497         |

THE STRUCTURE OF  $\text{CF}_3\text{NC}$   
=====

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The structure of the symmetric top trifluoromethylisocyanide has been determined by the combined use of Electron Diffraction intensities and the rotational constant  $B$ , determined by microwave spectroscopy.

The  $r_{\text{av}}$ -structure is:

CF:  $1.324(1)\text{\AA}$ , C-N:  $1.407(3)\text{\AA}$ , N=C:  $1.171(3)\text{\AA}$  and  
 $\angle\text{FCF}: 108.8^\circ(1)$ .

Analysis of the excited low-lying degenerate modes yields values of the Corioli coupling constants in accordance with the values determined from a normal coordinate analysis.

The well resolved quadrupole hyperfine structure of low- $J$  lines permitted a determination of the quadrupole coupling constant ( $1.06\text{ MHz}$ ), the largest coupling constant determined for an isocyanide so far.

The dipole moment has been determined to be  $1.153(20)\text{D}$ .

MICROWAVE AND MILLIMETER WAVE SPECTRUM OF DIAZIRINE  
ROTATIONAL AND HYPERFINE INTERACTIONS ANALYSIS

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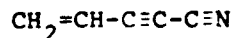
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Diazirine is the more stable cyclic isomer of diazomethane. This compound was first studied in the microwave range by PIERCE and Sr. DOBYNS [J. Amer. Chem. Soc. 84, 2651 (1962) ] who obtained approximate values of A, B and C through a rigid rotor analysis.

We have extended this study in the millimeter range up to 400 GHz. The a-type R- and Q-branch lines have been assigned in the ground vibrational state and accurate values of the rotational and centrifugal distortion constants have been obtained.

A careful analysis of the nuclear quadrupole hyperfine interaction has led to a discrepancy between the observed and calculated multiplets components frequencies and it has been necessary to include the spin-rotation interaction in the hamiltonian to obtain a good fit of all the experimental data. The derived coupling constants will be presented.

INTERSTELLAR SEARCH FOR 1-CYANO-BUT-3-EN-1-YNE,



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ABSTRACT

Previous Radio work has led to the detection of unexpectedly high abundances of long chain molecules in the interstellar medium. In particular  $\text{HC}_5\text{N}$ ,  $\text{HC}_7\text{N}$  and  $\text{HC}_9\text{N}$ . A number of synthetic schemes have been proposed to account for the generation of carbon chains in space: gas phase ion-molecule reactions, grain surface catalysis and circumstellar shell synthesis. In a number of these schemes significant amounts of partially unsaturated molecules such as  $\text{CH}_2=\text{CH}-\text{C}\equiv\text{C}-\text{C}\equiv\text{N}$  ( $\text{H}_3\text{C}_5\text{N}$ ) should accompany completely unsaturated species such as  $\text{HC}\equiv\text{C}-\text{C}\equiv\text{C}-\text{C}\equiv\text{N}$  ( $\text{HC}_5\text{N}$ ).

$\text{H}_3\text{C}_5\text{N}$  has been synthesized in our laboratory, its microwave spectrum analysed and a preliminary radio search carried out in sources rich in  $\text{HC}_5\text{N}$ . The results indicate that in TMCl, which is particularly rich in  $\text{HC}_5\text{N}$ , the upper limit for the  $\text{H}_3\text{C}_5\text{N}/\text{HC}_5\text{N}$  ratio is ca. 1/12.



## INFRARED DIODE LASER SPECTROSCOPY OF FREE RADICALS AND IONS

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The use of infrared lasers as light sources has greatly extended our knowledge of the structure of free radicals, ions and other transient molecules in the gas phase. Early studies used fixed frequency gas laser sources in the mid and far infrared and the Zeeman effect to tune transitions into resonance with the laser (Laser Magnetic Resonance). More recently diode lasers and other tunable devices have provided much greater frequency coverage without the need for a variable magnetic field.

We have developed a single beam diode laser spectrometer which can be operated under computer control for rapid scan spectroscopy. This instrument is used with a variety of different absorption sources. (i) A multiple pass cell in which radicals and transients are produced by atom-molecule reactions, (ii) a 3 m long d.c. discharge in a cooled tube where the laser is again multiple-passed through the discharge itself. This source has been used to generate  $\text{Ar}^+$ ,  $\text{CN}$ ,  $\text{HCl}^+$  and possibly  $\text{H}_3\text{O}^+$ . Relatively stable radicals like  $\text{NF}_2$  can be studied in a static cell. Calibration is provided by accurately measured spectra of stable molecules or by impressing  $\text{CO}_2$  laser emission lines on the spectra (this same technique is used to assign FIR laser transitions from diode laser spectra). Some recent results on free radicals and transient species recorded with the spectrometer and sources described above will be presented.

High Resolution Infrared Investigation of  $\text{H}_2\text{Si}^{79}\text{Br}$  in the  
 $\nu_2/\nu_3$  Region Near  $950\text{ cm}^{-1}$

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The FT infrared spectrum of monoisotopic  $\text{H}_2\text{Si}^{79}\text{Br}$  has been recorded with a resolution of  $0.0045\text{ cm}^{-1}$  in the  $800$  to  $1050\text{ cm}^{-1}$  region covering the fundamentals  $\nu_2$  and  $\nu_3$ .

A rotational analysis has been performed, and approximately 4000 lines have been fitted with a s.d.  $\sigma(J,K)$  of  $\sim 7 \times 10^{-4}\text{ cm}^{-1}$ .

The fundamentals  $\nu_2$ ,  $929.75\text{ cm}^{-1}$ , and  $\nu_3$ ,  $946.39\text{ cm}^{-1}$ , are strongly coupled by Coriolis x, y interaction, the  $k=3, l=0$  and  $k=2, l=-1$  levels coming almost to resonance. Two parameters,  $W+W'J'(J'+1)$  account for the gross effects of the  $1(1,1)$  resonance, and additional allowance has been made for  $1(2,2)$  resonance within  $\nu_3$ . Locally the  $\nu_3 = 1, k_1 = +2$  and  $-3$  levels are affected by  $1(2,-1)$  resonance, and the  $k_1 = -13$  and  $-14$  levels are involved in rotational  $1(1,1)$  type resonance with  $2\nu_3$  near  $859\text{ cm}^{-1}$ , crossing occurring for  $k_1 = -13$  between  $J' = 17$  and  $18$ .

A set of accurate parameters of the  $\nu_2 = \nu_3 = 1$  states and improved data for the ground state will be presented.

## The $\nu_1$ Fundamental Band of $D_2CO$ by Diode Laser Spectroscopy

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and

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The infrared spectra of formaldehyd,  $H_2CO$  and  $D_2CO$ , have been studied intensively by many spectroscopists with various high resolution spectrometers. However, strangely enough, the two fundamentals of  $D_2CO$ , the C-D stretching vibration  $\nu_1$  and  $\nu_5$ , have not been analysed with sufficiently high resolution. In the present study we have measured by a tunable diode laser spectrometer more than 1000 lines in the region of 2026-2087  $cm^{-1}$ , with Doppler limited resolution. The accuracy of the measurements is about 0.001  $cm^{-1}$ .

About 400 lines out of 1000 were assigned to the  $\nu_1$  fundamental band. The  $\nu_1=1$  state was found to be strongly perturbed by other states, probably  $(\nu_3=1, \nu_4=1)$  and  $(\nu_3=1, \nu_6=1)$  states. Although the complete analysis of the  $\nu_1$  band is hindered by this perturbation, we could determine the band origin,  $\nu_0=2060.917(1) cm^{-1}$ , and obtained the rotational constants in the  $\nu_1=1$  state to be

A= 140 263(38) MHz, B= 32 109(20) MHz, and C= 25 350(20) MHz.

Using the combination differences for the ground state together with the published microwave data, we have improved the molecular parameters in the ground vibrational state.

We are in the process to measure the  $\nu_5$  band by the diode laser to complete the analysis of the six fundamentals with high resolution. The diode laser spectra of the  $\nu_1$  and  $\nu_5$  bands are being extended by FT Bomem-Spectrometer of the Department of Physics, University of British Columbia.

THE VISIBLE WATER VAPOR SPECTRUM  
BETWEEN 13 500 AND 23 000  $\text{cm}^{-1}$

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Using the high resolution McMath Fourier transform spectrometer built by J. Brault associated with a White cell allowing very long path lengths (up to 430 m), several spectra of water vapor have been recorded between 13 500 and 23 000  $\text{cm}^{-1}$ . About 4 600  $\text{H}_2\text{O}$  lines have been observed among which about 3 200 lines belonging to 39 vibration-rotation bands have been assigned. The precision on the line positions is varying from  $0.3 \times 10^{-3} \text{ cm}^{-1}$  for the strongest and well isolated lines to  $25 \times 10^{-3} \text{ cm}^{-1}$  for the weakest ones (0.5 % of absorption at the center of the line).

About 600 experimental intensities have been obtained using either the equivalent width or the central depth of the lines : transitions as weak as  $10^{-26} \text{ cm}^{-1}/\text{molecule cm}^{-1}$  have been observed and measured. Many vibro-rotational levels have been determined from the wavenumbers of the observed transitions and some preliminary results concerning the theoretical calculation of these levels will be presented.

STRENGTHS AND WIDTHS OF N<sub>2</sub>O LINES FROM FOURIER TRANSFORM MEASUREMENTS :  
TEMPERATURE DEPENDENCE OF THE AIR-BROADENING COEFFICIENTS

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The line intensities have been measured by F.T. spectroscopy in four transitions of N<sub>2</sub>O near 4 μm and 8 μm. The band intensities and the rotationless dipole matrix elements have then been obtained. The uncertainty on both line and band strengths determinations is nearly 3 percent.

From the same experiments, the self, N<sub>2</sub> and O<sub>2</sub>-broadened linewidths have been measured at the two limit tropospheric temperatures, 295 and 220 K. The accuracy is also approximately 3 percent.

The air-broadened linewidths have then been derived for the two considered temperatures.

These experimental data have been compared to the values calculated by using an improved theoretical model. From this comparison the optimal conditions of the calculation were derived and then applied for several intermediate temperatures. At last, a simple relation is proposed in order to account for the temperature dependence of line widths.

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Tridiagonal Fermi-Resonance Structure in the Isolated  
CH-Stretching Overtones of Fluorinated Hydrocarbons and  $\text{CD}_3\text{H}$

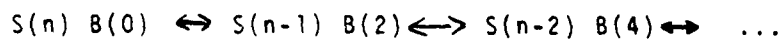
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Laboratorium für Physikalische Chemie

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The spectra of  $\text{CF}_3\text{H}$ ,  $\text{CD}_3\text{H}$ ,  $\text{C}_4\text{F}_9\text{H}$  and further  $\text{C}_n\text{F}_m\text{H}$  compounds have been recorded on a BOMEM DA.002 at high resolution (up to  $0.004\text{ cm}^{-1}$  apodized resolution) in the range between  $1000\text{ cm}^{-1}$  and  $14000\text{ cm}^{-1}$ , paying particular attention to the CH-stretching band systems. The analysis of these spectra reveals extensive Fermi-Resonance structure, which can be analyzed in terms of a simple model, involving only tridiagonal coupling between the states



( $S(n) B(m)$  indicates  $n$  quanta in the CH-stretching and  $m$  quanta in the CH-bending vibration.) The dynamics of this coupling is discussed also in relation to time-dependent intramolecular processes and further couplings that are induced by this Fermi-Resonance, and in relation to possible mechanisms for the IR-multiphoton excitation of polyatomic molecules.

HIGH RESOLUTION INFRARED AND MICROWAVE SPECTRA OF THE  
HYDROGEN FLUORIDE DIMER

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The hydrogen fluoride dimer has the structure,  $H_a-F \cdots H_b-F$ , where the  $H_a F F$  angle is about  $113^\circ$  and  $H_b$  is nearly collinear with the pair of fluorine atoms (1,2,3). The molecule can tunnel via a  $C_{2v}$  intermediate state to an equivalent structure and as a result the energy levels of each vibrational state are doubled.

The rotational structure in the HF stretching bands of  $(HF)_2$  has been studied with nearly Doppler-limited resolution using a tunable difference-frequency spectrometer and a long path cell held at low temperatures and pressures. Two infrared bands are observed. The higher frequency band,  $\nu_1$ , arising primarily from the  $H_a-F$  stretching mode, is a hybrid band consisting of a strong b-type perpendicular component and a weak a-type parallel component. For  $\nu_1$  the perpendicular subbands ( $\Delta K$ )K=2,1,0,-1,-2, and -3 as well as the K=0 subband of the parallel component have been assigned. The lower frequency band,  $\nu_2$ , due mainly to the  $H_b-F$  stretching vibration, is two to three times stronger than  $\nu_1$ , and only a-type transitions have been observed for this band. The K=0 and 1 subbands have been assigned for  $\nu_2$ . A non-pressure-dependent broadening of the lines of this band to about twice the Doppler width, is observed, and this effect is attributed to vibrational predissociation.

The tunneling-rotation microwave spectrum of  $(HF)_2$  and  $(DF)_2$  has been obtained at  $-70^\circ C$  and the line assignment has been extended up to K=2 and to considerably higher J than previous studies (1,3). In addition, the spectra of both HFDF and DFHF have been assigned in the ground state; DFHF for the first time.

In addition to the complications arising from the tunneling splitting, the molecule exhibits quasi-linear behavior, and it is necessary to fit each K level separately to obtain a set of effective rotational constants. The excited vibrational inversion splitting in  $(HF)_2$  for K=0 in  $\nu_1$  is 6462(8) MHz and that for  $\nu_2$  is 6998(12) MHz, about a third that of the ground state, 19747.04(2) MHz. An effective value for the A rotational constant has been obtained for the ground state with the aid of combination differences. This constant for the lower tunneling level is  $38.3039 \text{ cm}^{-1}$ , and, for the upper level, A is  $38.7442 \text{ cm}^{-1}$ .

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F



High Resolution Infrared Spectra of  $^{13}\text{C}^{12}\text{CH}_2$   
and  $^{13}\text{C}_2\text{H}_2$  at 13.7 Microns

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The infrared spectra of the carbon-13 enriched acetylene in the region  $630 - 830 \text{ cm}^{-1}$  have been recorded with the Fourier spectrometer at the University of Oulu /1/. The resolution was  $0.0045 \text{ cm}^{-1}$  and the accuracy of the line positions was about  $\pm 3.0 \times 10^{-5} \text{ cm}^{-1}$ .

The analysis of the bending fundamental of  $^{13}\text{C}^{12}\text{CH}_2$  and  $^{13}\text{C}_2\text{H}_2$  yielded the following results

		$^{13}\text{C}_2\text{H}_2$	$^{13}\text{C}^{12}\text{CH}_2$
$\nu_0$	$[\text{cm}^{-1}]$	728.35172(5)	729.37832(6)
$B_0$	$[\text{cm}^{-1}]$	1.1195699(13)	1.148458(2)
$D_0$	$[\text{cm}^{-1} \times 10^{-6}]$	1.4829(6)	1.5541(12)
$-\alpha_5 + \gamma_{55} + \gamma_{55}^{55}$	$[\text{cm}^{-1} \times 10^{-3}]$	1.84630(15)	1.9962(2)
$\beta_5$	$[\text{cm}^{-1} \times 10^{-8}]$	2.017(9)	2.26(2)
$q_5^0 + q_{55}$	$[\text{cm}^{-1} \times 10^{-3}]$	-4.2654(2)	-4.4826(3)
$\mu_5$	$[\text{cm}^{-1} \times 10^{-8}]$	3.221(14)	3.57(3)
Data		116	106
STD		$2.4 \times 10^{-4}$	$3.1 \times 10^{-4}$

The vibrational, vibration-rotation coupling and centrifugal constants for the excited vibrational states  $v_5 = 2$  and  $v_4 = v_5 = 1$  have been derived using the vibration-rotation energy matrix.

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THE  $3\nu_2$  BAND OF  $\text{CH}_3\text{D}$ : ROTATIONAL ANALYSIS, LINE INTENSITIES,  
AND PRESSURE-BROADENING COEFFICIENTS

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An extensive laboratory study undertaken with the high-resolution Fourier Transform Spectrometer and White cell at the Observatoire de Meudon in the region between 5000 and 10,000  $\text{cm}^{-1}$  has led to the identification of a number of new rotation-vibration bands of monodeuterated methane. One of these bands is centered near 6425  $\text{cm}^{-1}$  and was recently identified in the spectra of Saturn, Titan, and Uranus. We present our detailed rotational analysis of this band and derive constants of rotation. Complications due to severe local perturbations and their influence on the derived constants are discussed. Evidence that this band forms a vibrational series with  $\nu_2$  and the 9613 Å band is outlined, suggesting the vibrational assignments of the 6425  $\text{cm}^{-1}$  and 9613 Å bands are  $3\nu_2$  and  $5\nu_2$ , respectively.

Because of its importance to solar system observations, we have recorded additional high-resolution spectra of the 6425  $\text{cm}^{-1}$  band with the laboratory Fourier Transform Spectrometer and White cells at Kitt Peak National Observatory under self-broadened and foreign gas-broadening conditions appropriate to planetary environments. Preliminary results which describe line intensities and pressure-broadening coefficients for  $\text{N}_2$ ,  $\text{H}_2$ , and He, as well as for self-broadening, determined using an algorithm which fits observed spectral lines with a Voigt profile, are shown.

This research is supported in part by NASA through research grant NSG-7499.

INFRARED STUDY OF A  $\text{SiH}_4$  PLASMA AT 5  $\mu$

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A new experimental set-up has been built to observe a silane plasma ; among the products of the dissociation of  $\text{SiH}_4$  due to electron impacts, the most probable radicals are  $\text{SiH}$ ,  $\text{SiH}_2$  and  $\text{SiH}_3$ . In a preliminary experiment (1) of high resolution absorption and emission spectroscopy in the 1800 - 2300  $\text{cm}^{-1}$  range, the 1-0 and 2-1 bands of the  $\text{SiH}$  free radical have been weakly observed.

In order to improve the observation of these radicals, a 2.5 meter long reactor has been built, containing a White type cell. In a preliminary stage a diode laser spectrometer is used to check the global efficiency of the apparatus through the optimisation of several parameters (plasma geometry, r.f. frequency and power coupling). Then the excitation conditions are monitored continuously by this diode laser allowing the adjustments of pressures and flows of  $\text{SiH}_4$  and possibly its vector gas ( $\text{H}_2$ ) as well as the radio frequency power parameters. Simultaneously the whole spectrum is recorded with the Fourier transform interferometer.

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THE  $\nu_1$  BAND OF  $^{14}\text{N}^{16}\text{O}_2$   
LINE POSITIONS AND INTENSITIES

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High resolution Fourier transform spectra (resolution of about  $5 \times 10^{-3} \text{ cm}^{-1}$ ) have been used to measure precisely the line positions and intensities of the  $K_a = 0 - 12$  stacks of the  $\nu_1$  band of  $^{14}\text{N}^{16}\text{O}_2$  in the  $1240 - 1500 \text{ cm}^{-1}$  region.

Using an hamiltonian which takes explicitly into account the Coriolis resonances between the (001) state and the (100) and (020) states we were able to reproduce satisfactorily the rotational energy levels of the three interacting states {(020), (100), (001)} of  $^{14}\text{N}^{16}\text{O}_2$ . An improved set of spin-rotation, rotational and Coriolis coupling constants were determined for these three interacting states. In particular we have been able to determine, for the (100) state, asymmetric dependant constants such as (B-C) and  $(\epsilon_{bb} - \epsilon_{cc})$  which could not be determined in the previous work concerning the  $\nu_1$  band, by Laurin and Cabana [1].

Moreover, individual intensities of transitions belonging to the  $\nu_1$  band were measured, leading to the precise determination of the vibrational part of the transition moment operator of the  $\nu_1$  band together with 5 correcting rotational terms appearing in the expansion of this operator.

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# INFRARED DOUBLE RESONANCE SPECTROSCOPY OF METHANE AND THE LOCAL MODE MODEL

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The stretching vibrational spectrum of methane has been calculated on the basis of the local mode model. Due to the large anharmonicity of the C-H stretch, this approach gives a very good description of the stretching levels of methane, even in the low energy region. Many infrared active stretching bands, including the very first ones, are well accounted for.

Little information being available concerning the infrared-inactive levels, infrared double resonance experiments were carried out to determine the positions of the unknown E and  $A_1$  components of the  $2\nu_3$  manifold of methane in the  $6000\text{ cm}^{-1}$  region.

Two separately tunable high-power infrared dye lasers were shifted to the  $3.3\text{ }\mu\text{m}$  region by two successive stimulated Raman scatterings in hydrogen gas, thus providing the pump and probe beams.

Several rotational lines of the  $\nu_3 \rightarrow (2\nu_3, A_1)$  and  $\nu_3 \rightarrow (2\nu_3, E)$  bands were recorded, and the measured vibrational energies of the  $A_1$  and E levels ( $5968$  and  $6044\text{ cm}^{-1}$  respectively) were found to be quite close to the predicted values.

Rovibrational Spectra of  $\text{CF}_3^{35}\text{Cl}$  in the  $\nu_4$ ,  $2\nu_4$ ,  $3\nu_4$   
and  $\nu_4 + \nu_5$  Ranges

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The infrared spectra of monoisotopic  $\text{CF}_3^{35}\text{Cl}$  have been recorded with a resolution of 0.02 to 0.04  $\text{cm}^{-1}$  in the region of  $\nu_4$ ,  $2\nu_4$ ,  $3\nu_4$  and  $\nu_4 + \nu_5$ , near 1200, 2400, 3600 and 1800  $\text{cm}^{-1}$  respectively. Rovibrational analyses have been performed by band contour simulations, starting from polynomial fits of Q branches.

- A simultaneous  $l(2,2)$  and  $l(2,-1)$  resonance similar to that recently observed by Hirota et al. for  $\nu_3$  of  $\text{CF}_3$  affects mainly the  $K' \leq 3$  levels of  $\nu_4$ .
- The K structure of both  $2\nu_4$  components,  $l = 0$  and  $l = \pm 2$ , has been evaluated, the assignment of  $2\nu_4^{\pm 2}$  following from the observation of  $3\nu_4^{\pm 1}$ .
- Due to the substantial size of  $[(A_{444} - A_0) - (B_{444} - B_0)]$ ,  $3\nu_4^{\pm 1}$  exhibits a characteristic head-type structure of the  $P_Q$  branches at higher frequencies from  $\nu_0$ .
- The intensity of the pseudoperpendicular component  $(\nu_4^{\pm 1} + \nu_5^{\pm 1})$  dominates over that of the  $l = \pm 2$  component. In contrast to  $(\nu_5^{\pm 1} + \nu_6^{\pm 1})$ , it exhibits a substantial  $A_1A_2$  resonance,  $R \approx 2.5 \text{ cm}^{-1}$ .

ETUDE DU SPECTRE INFRAROUGE DU SILANE DANS LA REGION DE 830 A 1 040  $\text{cm}^{-1}$ .  
ANALYSE DU NIVEAU DE BASE, ET DES NIVEAUX  $v_2 = 1$  et  $v_4 = 1$ .

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Le spectre d'absorption infrarouge des bandes  $v_2$  et  $v_4$  du Silane a été enregistré sur le spectromètre à transformée de Fourier du Laboratoire de Spectronomie Moléculaire de PARIS. L'étude du niveau de base et des niveaux  $v_2$  et  $v_4$  a été réalisée à partir de l'Hamiltonien de CHAMPION développé au 4ième ordre d'approximation.

Pour l'étude du niveau de base du  $^{28}\text{SiH}_4$ , 590 différences de fréquences ont été utilisées pour déterminer les 3 paramètres scalaires de ce niveau, les 3 paramètres tensoriels sont fixés aux valeurs déterminées par l'analyse des transitions micro-onde. Les différences de niveau de base sont reproduites avec une précision de  $0.00019 \text{ cm}^{-1}$ .

L'étude des niveaux de la diade  $v_2$  et  $v_4$  a été réalisée à partir de 786 niveaux rovibrationnels. Les 29 paramètres de l'Hamiltonien développé au 4ième ordre relatifs aux états  $v_2 = 1$  et  $v_4 = 1$  ont été déterminés. L'écart type obtenu sur les 786 niveaux est de  $0.001 \text{ cm}^{-1}$ .

L'analyse des bandes  $v_2$  et  $v_4$  des deux espèces isotopiques  $^{29}\text{SiH}_4$  et  $^{30}\text{SiH}_4$  est en cours de réalisation. La qualité des résultats déjà obtenus est comparable à celle de l'isotope principal.

THE MICROWAVE SPECTRUM OF CYANOPHOSPHA-BUTADIYNE



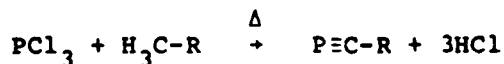
M. Durrant, H.W. Kroto, D. McNaughton and J.F. Nixon

School of Molecular Sciences

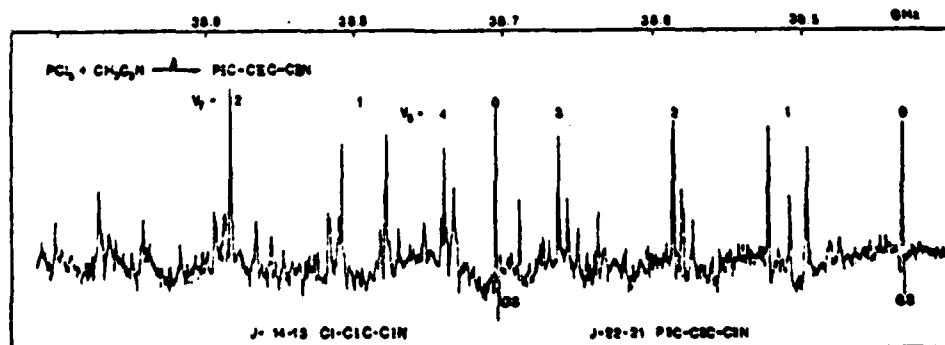
University of Sussex Falmer Brighton BN1 9QJ

ABSTRACT

Using flow-pyrolysis techniques the phosphalkynes  $\text{R}-\text{C}\equiv\text{P}$  ( $\text{R} = \text{HC}\equiv\text{C}-$ ,  $\text{Ph}-$ ,  $\text{N}\equiv\text{C}-$ ) have been produced by co-pyrolysis of the methyl group containing molecules ( $\text{R}-\text{CH}_3$ ) and  $\text{PCl}_3$  according to the scheme



$\text{N}\equiv\text{C}-\text{C}\equiv\text{C}-\text{C}\equiv\text{P}$  has been generated for the first time by this method, and its vibrationally rich microwave spectrum has been assigned up to  $\nu_9=4$ , and  $\nu_8=2$ . A number of other linear molecules were identified in the pyrolysis products. This study has been successful because of the excellence of microwave spectroscopy in detecting linear molecules like  $\text{N}\equiv\text{C}-\text{C}\equiv\text{C}-\text{C}\equiv\text{P}$  with relatively large dipole moments.





Microwave Spectrum of Silyl acetylene  
in the  $3\nu_{10}$  state

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Silyl acetylene is a  $C_{3v}$  symmetry type molecule whose microwave rotational spectra have been studied in the ground vibrational state [1,2], in the  $\nu_{10}$  [1] and  $2\nu_{10}$  [3] states.

The measurements have been extended to the  $3\nu_{10}$  vibrational manifold of the lowest bending mode ( $\nu_{10} : 220 \text{ cm}^{-1}$ )

Many transitions from  $J : 0 \rightarrow 1$  to  $J : 11 \rightarrow 12$  up to 117 GHz have been observed with Stark and video spectrometers, for which high sensitivity was required because of the low dipole moment of the molecule.

The assignment and analysis, which should have been straight-forward with the knowledge of constants derived from the lower states, was perturbed by interactions with other vibrations levels. In particular, it was impossible to derive a unique set of constants for the  $l = \pm 1$  and  $l = \pm 3$  states.

The diagonalization treatment of the hamiltonian yields two sets of parameters, showing large variations for the two states, especially for the centrifugal distortion constants.

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## The Microwave Spectrum of Ethylamine-Gauche

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The microwave spectrum of the ground state of the normal species of gauche-ethylamine  $\text{CH}_3\text{CH}_2\text{NH}_2$  and that of -NHD, -NDH as well as -ND<sub>2</sub> isotopic species were measured and assigned. The ground state splits into four substates due to two internal large amplitude motions: inversion (s and a) and internal rotation (o and e) about the CN axis. Intersystem transitions due to tunneling as well as vibrational rotational perturbations affect not only the absorption frequencies but also the dipole moment and NQHFS. The rotational constants for the two symmetrical (s) and the two antisymmetrical (a) inversion states were fitted. The energy splitting due to inversion was determined (in MHz) as  $\Delta\nu_{\text{inv}} = 1\,391.39 \pm 0.19$  and that due to internal rotation as  $\Delta\nu_{\text{tors}} = 1\,170.58 \pm 0.18$ . The cis barrier separating the two equivalent torsional states was calculated as  $690\text{ cm}^{-1}$  and the inversion barrier between the inversion states was calculated as  $1400\text{ cm}^{-1}$ , both using the Dennison Uhlenbeck model. The gauche form was observed to be energetically higher than the trans form by  $110 \pm 50\text{ cm}^{-1}$ . The dipole moment could only be fitted by taking into account the internal motions yielding (in Debye)  $\mu_{\text{a}}^{\text{eff}} = 0.11 \pm 0.01$ ,  $\mu_{\text{b}}^{\text{eff}} = 0.65 \pm 0.01$ ,  $\mu_{\text{c}}^{\text{eff}} = 1.014 \pm 0.015$ .

High Resolution Rotational Zeeman effect  
Studies of Small Open Chain Molecules

D.HOBNER, W.H.STOLZE, and D.H.SUTTER\*

The rotational Zeeman effect of Aethylchloride, Nitrous Acid, Cyanoacetylene and Vinylcyanide has been investigated under high resolution.

Our results will be discussed in view of local increments to the molecular magnetic susceptibility tensor and the molecular electric quadrupole moments 1, 2.

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Rotational Zeeman Effect Studies  
of Aromatic Systems.

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By the use of a high resolution superheterodyne bridge spectrometer [1], [2] the investigation of the rotational Zeeman effect of substituted aromatic systems including up to two quadrupole nuclei became possible. Our recent results obtained for Trifluorobenzene, Pyrazole and Imidazole will be compared with those of related rings and with quantum chemical calculations of the  $\pi$ -electron densities [3].

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Z.Naturforsch. 36a, 886 (1981).

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Isotope effects of heavy atoms in diatomic molecules

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Using the high resolution techniques of microwave and laser spectroscopy and their combination in double resonance experiments the isotope effects to very high order can be studied. For heavy atoms the influence of the breakdown of the Born-Oppenheimer approximation on the molecular spectra is expected to be almost unobservable because the ratio of the electron to the nuclear mass and the relative changes of the nuclear masses by isotope substitution are very small. The observed isotope effects can be unambiguously attributed to the influence of the finite nuclear size and its isotope variation.

Examples are given for the molecules PbO, PbS and HgH. This new interpretation gives an exciting molecular quantity: the total electron density at the nucleus under study as a function of internuclear distance.

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Title of poster:

The Spectra of  $^{74}\text{Ge}^{16}\text{O}$  and  $^{74}\text{Ge}^{18}\text{O}$  in the Vacuum  
Ultraviolet Region

Abstract

The spectra of the isotopic molecules  $^{74}\text{Ge}^{16}\text{O}$  and  $^{74}\text{Ge}^{18}\text{O}$  have been studied in the vacuum ultraviolet region by the flash absorption technique.

The vibrational numbering of the  $E^1\Sigma^+-X^1\Sigma^+$  system has been settled and rotational constants of the upper state derived. Further, several bands in the region 1220-1550Å have been observed, most of which have been rotationally and vibrationally analyzed.

From one of the perturbations observed, rotational constants of the perturbing state could be derived.

Dr O. Appelblad

Prof. A. Lagerqvist

H-ex på FyL S. Fredin

ACCURATE MEASUREMENTS OF COLLISIONAL CROSS SECTIONS OF BaO ( $A^1\Sigma^+$ ) WITH Ar.

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In another contribution to this colloquium we present a theory of relaxation. In this paper we apply that theory to RET and RET-VET and quenching processes of BaO ( $A^1\Sigma^+$ ) in Ar.

BaO is prepared in a specific rovibronic level by cw-laser excitation after being produced in a Broida-type oven. Fluorescence is detected with so low a resolution that rotational structure is not seen.

Using the well-known optical lifetime we extract from these measurements accurate absolute values for the following cross sections:

1.  $\sigma_{rot}$ , total cross section for rotational relaxation from the excited level;
2.  $\sigma_{vib}$ , idem for vibrational relaxation;
3.  $\sigma_{v_i^i \rightarrow v_f^f}$ , cross section for specific  $v_i^i \rightarrow v_f^f$  transition;
4.  $\sigma_{quen}$ , total cross section for quenching.

All these can be derived from *relative* intensity measurements in dependence of pressure. Preliminary experiments indicate that with this experimental method a considerable increase in accuracy can be obtained compared to previously published results.

## HIGH RESOLUTION UV LASER SPECTROSCOPY OF SH

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The hyperfine and spin-rotation structure of SH in the first excited electronic state  $A^2\Sigma_1^+$ ,  $v' = 0$  has been measured by laser induced fluorescence detection in a molecular beam set-up. The SH radicals were produced in the reaction



in front of the molecular beam source. The  $A^2\Sigma_1^+$ ,  $v' = 0 \leftarrow X^2\Pi_2$ ,  $v'' = 0$  transitions at 324 nm were induced by c.w. UV radiation from a ring dye laser with intracavity frequency doubling in a  $LiIO_3$  crystal.

The  $\rho$ -doublet and hyperfine splittings have been measured for  $N' = 0$  up to  $N' = 9$ . From a least squares fit the spin-rotation constant  $\gamma$ , its centrifugal distortion  $\gamma_D$  and the hyperfine constants  $b$  and  $c$  were obtained (in MHz):  $\gamma = 9506.7 \pm 0.6$ ,  $\gamma_D = 0.870 \pm 0.013$ ,  $b + \frac{c}{3} = 898.5 \pm 1.0$ ,  $c = 51.1 \pm 2.6$ .

The linewidths increased strongly with  $N'$  indicating the presence of predissociation. After correcting for the Doppler contribution to the linewidth due to the molecular beam divergence a natural lifetime was deduced ranging from 3.2 ns for  $N' = 0$  to 1.1 ns for  $N' = 9$ . Probably the predissociation is caused by the interaction with the repulsive  $^4\Sigma^-$  state crossing  $A^2\Sigma_1^+$  between  $v' = 0$  and  $v' = 1$ .



$\Lambda$  -TYPE DOUBLING AND TERM FORMULAE FOR A  
 $^5\Pi$  STATE IN THE INTERMEDIATE CASE BETWEEN  
HUND'S CASES (a) AND (b)

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Explicit expressions valid for all values of  $Y$  intermediate between Hund's cases (a) and (b) are obtained for the multiplet term formula and for the width of the  $\Lambda$ -type doubling of a  $^5\Pi$  state. Good agreement between experimental data and the theory of the  $^5\Pi_1$  state of NdO molecule has been found.

SPECTRE DRASC DE CO<sub>2</sub> A HAUTE TEMPERATURE  
RESULTATS EXPERIMENTAUX ET SIMULATION THEORIQUE

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Résumé

La Diffusion Raman Anti-Stokes Cohérente (DRASC) est une méthode spectroscopique qui apporte de nombreux avantages par rapport à la spectroscopie Raman conventionnelle. En particulier, la DRASC est utilisée pour les diagnostics de combustion. CO<sub>2</sub> étant un important produit de combustion, nous avons effectué une étude spectroscopique de cette molécule à différentes températures. Ce travail fait suite à une étude à température ambiante [1, 2].

Un spectre de CO<sub>2</sub> a été enregistré dans la région spectrale de 1160-1520 cm<sup>-1</sup> à 800 K avec un montage DRASC commercial. La résolution est approximativement de 0,06 cm<sup>-1</sup>. Les faisceaux laser excitateurs étaient colinéaires avec des polarisations croisées pour annuler le fond non résonnant. Cette région spectrale est celle où se trouvent les deux bandes intenses  $\nu_1$  et  $2\nu_2$  perturbées par la résonance de Fermi. Nous avons observé la structure rotationnelle de ces bandes pour l'espèce principale <sup>12</sup>C<sup>16</sup>O<sub>2</sub> ainsi que pour les espèces isotopiques <sup>13</sup>C<sup>16</sup>O<sub>2</sub>, <sup>12</sup>C<sup>16</sup>O<sup>18</sup>O et <sup>12</sup>C<sup>16</sup>O<sup>17</sup>O. De plus, nous avons attribué de nombreuses bandes chaudes, en particulier, celles dont les états de départ appartiennent aux groupes de polyades ayant  $2\nu_1 + \nu_2 = 3, 4$  ou  $5$ ,  $\nu_3 = 0$ , par exemple, 03301, 04401, 05501, 13301, 21102. La plupart de ces bandes n'avait jamais été observée. Ces données devraient permettre une amélioration des paramètres de certains états.

En DRASC, il est nécessaire d'effectuer une simulation du spectre expérimental pour attribuer sans ambiguïté les raies. Ce calcul théorique a été effectué comme dans la référence [2] pour le spectre à température ambiante. Les spectres expérimental et théorique, ainsi que les détails de l'interprétation seront présentés.

[1] - N. Papineau and M. Péalat : "CARS spectroscopy of CO<sub>2</sub>" in Proceedings of the 8th International Conference on Raman Spectroscopy, Bordeaux (France), sept. 1982, Ed. J. Lascombe and Pham. V. Huong, Wiley and Sons, New-York.

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REVISED ANALYSIS OF THE STRUCTURE OF THE  $\nu_1$  BAND  
OF METHANE BASED ON HIGH RESOLUTION CW CARS SPECTRA

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The CARS Spectrum of the  $\nu_1$  band of  $^{12}\text{CH}_4$  at a pressure of 14 mbar was recorded using cw excitation in the cavity of a ring argon ion laser. The analysis of the intensity profile of the observed spectrum led to the detection of inconsistencies with the hitherto proposed (1,2) calculated positions of transitions and energy levels with  $J = 7$  to  $J = 10$  and to a relocation of the corresponding lines. With the set of revised line positions the intensity contours not only of our CARS spectra, but also those of published stimulated Raman gain and loss spectra are well reproduced.

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J.Mol.Spectrosc. 93, 351 (1982)

## REALISATION D'UN LAMBDAMETRE.

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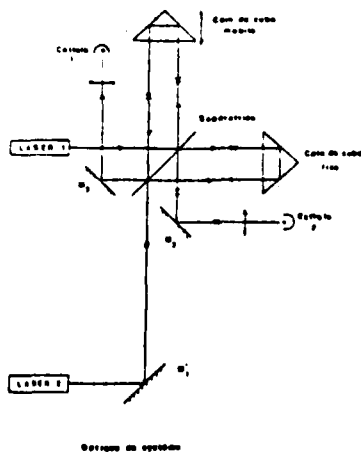
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Nous utilisons un double interféromètre de MICHELSON pour comparer la longueur d'onde inconnue d'un laser continu avec la longueur d'onde connue d'un laser de référence (Hélium-Néon stabilisé sur la raie d'absorption saturée "i" de l'iode à  $6\ 328\ \overset{\circ}{\text{Å}}$ ). Le système est conçu de façon à ce que la différence de marche soit identique pour chacun des deux faisceaux.

Le coin de cube mobile se déplace verticalement (sur une distance d'environ 1 mètre), dans une enceinte où l'on a réalisé le vide. Le mouvement du coin de cube, contrôlé par un microprocesseur est accéléré puis retardé dans les phases extrêmes du déplacement. Pendant ces deux phases, toutes les mesures utiles sont mémorisées. Une interpolation polynomiale permet le pointé des instants initial et final. Chaque cycle dure environ 3 secondes actuellement.

La qualité des résultats dépend essentiellement de l'alignement des deux faisceaux dans l'appareil. La précision relative varie actuellement entre  $10^{-8}$  et  $10^{-9}$ .



COURBES D'ENERGIE POTENTIELLE CALCULEES A LONGUE DISTANCE  
 POUR LES ETATS MOLECULAIRES DES DIMERES ALCALINS  $\text{Li}_2$ ,  $\text{Na}_2$   
 ET  $\text{K}_2$ , DISSOCIANT EN  $^2\text{S}_{1/2} + ^2\text{S}_{1/2}$  ET  $^2\text{S}_{1/2} + ^2\text{P}_J$

CALCULATED LONG RANGE POTENTIAL ENERGY CURVES FOR  
 MOLECULAR STATES OF  $\text{Li}_2$ ,  $\text{Na}_2$  AND  $\text{K}_2$  DISSOCIATING  
 IN  $^2\text{S}_{1/2} + ^2\text{S}_{1/2}$  AND  $^2\text{S}_{1/2} + ^2\text{P}_J$

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Les premiers coefficients non nuls du développement multipolaire de l'énergie d'interaction à longue distance entre deux atomes alcalins identiques X ( $X \in \{\text{Li}, \text{Na}, \text{K}\}$ ) sont calculés dans le cas où les deux atomes sont dans leur état fondamental  $^2\text{S}_{1/2}$  ainsi que dans le cas où un atome est dans l'état fondamental et l'autre est dans l'état excité  $^2\text{P}_J$  ( $J=1/2, 3/2$ ).

Les formules permettant l'évaluation des coefficients  $C_3$  et  $C_{2n}$  ( $n=3, 4, 5$ ) sont présentées. Elles sont toutes exprimées en fonction d'éléments de matrice du type  $\langle n\ell | r^k | n'\ell' \rangle$  où  $n\ell$  représente la fonction d'onde ns du fondamental ou np du premier état excité p et  $n'\ell'$  représente les fonctions d'onde des états excités. La fonction d'onde du fondamental ns est obtenue par une méthode de potentiel modèle (potentiel de Klapisch) tandis que les fonctions d'onde excitées sont choisies comme étant des fonctions de Witteraker d'indice  $\nu$  non entier déterminé à partir du spectre d'énergie expérimental de l'atome X. Les fonctions d'onde des états très excités pour lesquels l'énergie expérimentale n'est pas connue sont simplement représentées par des hydrogénéoïdes.

Pour les états dissociant en  $^2\text{S}_{1/2} + ^2\text{S}_{1/2}$  ( $X^1\Sigma_g^+$ ,  $^3\Sigma_u^+$ ) nous avons obtenu les résultats suivants :

coefficient molécule	$C_6$	$C_8$	$C_{10}$
	en $10^6 \text{Å}^6 \text{ cm}^{-1}$	en $10^8 \text{Å}^8 \text{ cm}^{-1}$	en $10^{10} \text{Å}^{10} \text{ cm}^{-1}$
$\text{Li}_2$	5.75	0.89	0.15
$\text{Na}_2$	8.18	1.39	0.26
$\text{K}_2$	22.47	4.8	1.30

L'étude similaire pour les coefficients  $C_3$ ,  $C_6$ ,  $C_8$  et  $C_{10}$  est en cours pour les états dissociant en  $^2\text{S}_{1/2} + ^2\text{P}_J$  ( $J=1/2, 3/2$ ).

Group Theoretical Treatment of Planar Internal Rotation in  $(\text{HF})_2$

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Separate group-theoretical treatments of the internal-rotation tunneling problem in the hydrogen fluoride dimer  $(\text{HF})_2$  have been carried out for two tunneling paths, using internal axis method (IAM) coordinate systems. One path is characterized by a trans intermediate configuration of  $C_{2h}$  symmetry, the other by a cis intermediate configuration of  $C_{2v}$  symmetry. It is found that when each of these tunneling paths is considered separately, then the symmetry species of vibrational, rotational, and internal-rotational energy levels and operators as well as the selection rules for electric dipole transitions obtained from a Longuet-Higgins permutation-inversion group treatment are identical with those obtained from a point group treatment based on the geometry of the intermediate (highest symmetry) configuration for that path. If both paths are considered simultaneously, a double group treatment appears to be required. All experimental observations to date are consistent with a trans intermediate configuration, but not with a cis intermediate configuration, in agreement with the tunneling path favored by chemical intuition.

ON CALCULATION OF VIBRATION-ROTATION ENERGIES AND  
POTENTIAL FUNCTION OF DIATOMIC MOLECULES

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H



THE EMPIRICAL GENERAL HARMONIC POTENTIAL  
FUNCTION OF ETHANE

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A total of 175 spectroscopic data, accumulated from 10 isotopic species of ethane, are used to define all 22 parameters of the harmonic potential function within narrow limits. Before calculation, numerous Fermi resonances have been identified and quantified through infrared and Raman spectroscopic studies of  $\text{CH}_3\text{CD}_3$  and its  $^{13}\text{C}$  isotopic species. This is an essential pre-requisite to such an investigation, without which a self-consistent empirical data set cannot be achieved, from which to determine physically meaningful force constants.

Comparison of the empirical force constants with those predicted by scaled *ab initio* calculations shows an excellent degree of correspondence in all force constants, and confirms that both approaches can lead to essentially identical results.

Calculated values of spectroscopic data of reliable quality are available. These should be of value to future spectroscopic investigation of isotopic ethanes and to resolving the many resonance perturbations which are present.

ON SOME NEW ASPECTS IN THE KIVELSON-WILSON-NILSEN  
THEORY OF VIBRATION-ROTATION STATES OF MOLECULES

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A B S T R A C T

A new approach has been developed, which enabled one to solve in the framework of the conventional Kivelson-Wilson-Nilsen theory some problems, which was considered to be inapplicable for this theory. It was shown, that the "inapplicability" of the conventional model of the Hamiltonian ( the conventional model is a Watson's Hamiltonian [1] with the potential function in the form of series expansion over vibrational coordinates) for some problems is due to only the neglecting of a number of terms in series expansions of the  $M_{\alpha\beta}$  values. The approach suggested gives the possibility of obtaining the effective rotational Hamiltonian without this limitation ( in fact summation of some infinite series expansions over vibrational coordinates has been made).

The approach developed was used for the analysis of different molecules. It was shown, in particular, that for the  $H_2O$ -type molecules, when a quantum number  $V_2$  increases, the "anomalous" behavior of rotational  $A$  and centrifugal  $\Delta_K$ ,  $H_K$ , etc.) constants is caused not by impossibility of expanding the potential function in Taylor series, but by rather small values of constants  $\omega_2$  and  $I_{zz}^0$ . It was shown there is no need to use the most complicated Hougen-Bunker-Johns model for describing correctly the rotational, centrifugal, unharmonic and other constants [ 2 ].

The approach developed is used for determining the unharmonic part of the potential function and the structure parameters of some molecules. When solving this problem formulas for spectroscopic constants obtained by means of analytical calculations with the help of computer were used.

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# INVERSE RAMAN SPECTROMETER USING A NARROW-LINE WIDTH HIGH-POWER LASER.

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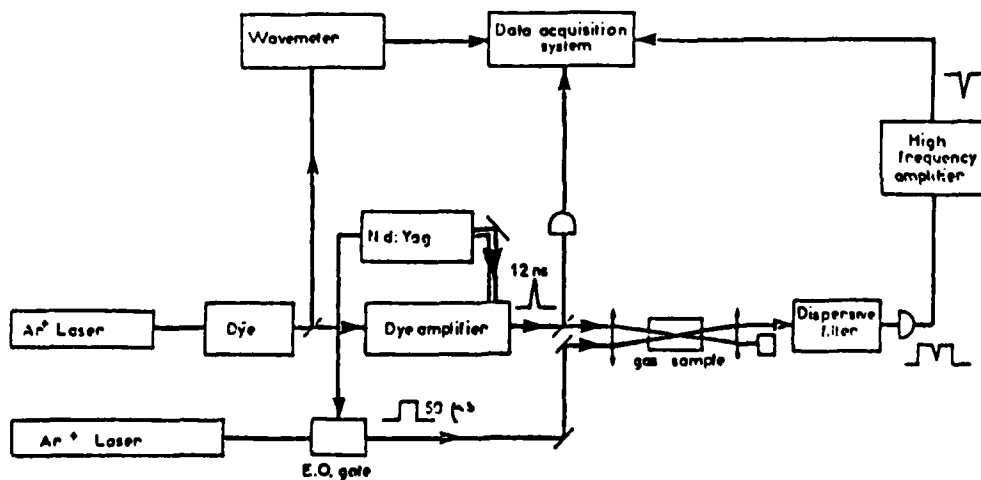
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A pulsed pump laser and a single mode cw probe laser are overlapped in a focus in the gas sample. The pulsed pump laser is obtained by amplifying an electronically scanned single mode cw dye laser in dye amplifiers pumped with a frequency-doubled Nd: YAG Laser. The output pulses have a power of 1MW and 12 ns duration at 10 pps repetition rate.

The probe laser is modulated by an electro-optic device in order to reduce the average power on the detector. The Raman absorption signal is detected on the probe laser by a photodiode and amplified before being stored in real time in a data acquisition system.

Applications to some diatomic and spherical top molecules will be presented.



A cw CARS SPECTROMETER WITH INTRACAVITY EXCITATION  
FOR HIGH RESOLUTION RAMAN SPECTROSCOPY

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A high-resolution CARS spectrometer consisting of a cw argon ion laser in ring configuration and a dye ring laser was constructed. The sample cell is inside the argon laser cavity which is actively stabilized to an iodine absorption line. The instrumental resolution is  $0.001 \text{ cm}^{-1}$  and at low pressures the observed linewidths are Doppler-limited.

With single mode powers of about 150 W at 514 nm and 100 to 200 mW of the dye laser CARS spectra of nitrogen, methane, ammonia, hydrogen sulfide, benzene, and allene were recorded.

The Q-branch of  $\text{N}_2$  can be reproduced by the molecular constants given by Bentsen (1), however, with reduced statistical error.

Recently a computer controlled data acquisition system has been installed.

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Avoided-Crossing Experiments in the Ground State  
of NO<sub>2</sub> and ClO<sub>2</sub>

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Zeeman spectroscopy of magic-doublet transitions offers the possibility to determine the diamagnetic properties of freely rotating paramagnetic molecules. We have previously applied this method to the vibrational ground state of ClO<sub>2</sub>, using low magnetic field strengths<sup>1)</sup>.

At higher fields, sometimes already above 0.5 T, the perturbation by interfering rotational Zeeman levels becomes increasingly important and the observed doublets may lose their magic behaviour by the growing influence of unpaired electronic magnetism. While this can be understood and formally described in detail by matrix-diagonalization techniques, it leads to undesired inhomogeneous line broadening with the effect that the doublet or one component thereof may become unobservable.

In fortunate cases, however, the complete avoided-crossing pattern<sup>2)</sup> lies within our accessible field-strength range of maximally 3 T where the high-field branches return to experimental observability regaining their magic behaviour. The availability of the complete avoided-crossing pattern was particularly important for NO<sub>2</sub>, where only few (unfortunately strongly correlated) rotational transitions exist in the suitable frequency range.

We have observed the field dependence of seven magic doublets of NO<sub>2</sub> and ten of ClO<sub>2</sub> in the frequency range between 10 and 180 GHz, using field strengths up to 2.6 T for  $|\Delta N|=1$  (P and R branch) transitions and up to 3 T for  $\Delta N=0$  (Q branch) transitions.

Some spectroscopic data and the evaluated molecular parameters will be presented.

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## Laser Spectroscopy of Samarium Oxide

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The electronic structure of most of the diatomic rare-earth oxides consist of numerous low-lying electronic states resulting from the high orbital angular momentum and spin multiplicities of open shell  $4f^N$  atomic states of the parent metal free ion.

Laser induced fluorescence techniques have been successfully employed in the PrO and CeO studies leading to low lying states energy level linkages (1,2). Ligand Field Theory has been a powerful tool in interpreting the electronic structure of these molecules and in predicting the configurational assignments for the low-lying electronic states of the diatomic rare-earth oxides. For most of the lanthanide monoxides the lowest-lying molecular states should arise from the  $(4f)^N 6S$  superconfiguration. However, quantitative Ligand Field calculations using Burn's rule estimates of orbital sizes predict the ground super configurations  $4f^7$  for  $E_uO$ ,  $4f^{14}$  for YbO and two low near lying super configurations  $4f^5 6S$  ( $\omega_e \approx 830 \text{ cm}^{-1}$ ) and  $4f^6$  ( $\omega_e \approx 680 \text{ cm}^{-1}$ ) for SmO.

Recent laser spectroscopy experiments have provided a beginning of testing of the Ligand Field predictions for Holmium and Ytterbium Oxides and for Lanthanum Fluoride (3).

We report here preliminary results from pulsed dye laser and C.W. laser induced fluorescence experiments which have provided energy linkages between some electronic lower states and vibrational frequencies of SmO which are consistent with the Ligand Field Theory predictions.

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International Colloquium on Diatomic Molecules, Oxford (1983)



HIGH RESOLUTION EMISSION SPECTRUM OF H<sub>2</sub> BETWEEN 77 AND 118 nm :

MOLECULAR CONSTANTS OF THE  $1\Pi_u$  STATES

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Although molecular hydrogen is one of the most studied and best known molecules, it may look surprising that its emission spectrum has never been analyzed at wavelengths shorter than 118 nm<sup>1</sup>, in which region the main part of the spectrum takes place. This is simply because the pressure of a few Torr in a conventional discharge gives rise to strong reabsorption of the entire spectrum at short wavelengths. On the contrary the use of a low pressure discharge in the presence of a magnetic field has allowed us to reduce greatly reabsorption and to observe emission lines down to about 77 nm. A preliminary analysis of the short wavelength range (<85 nm) has been reported recently<sup>2</sup>.

From the known absorption spectrum it is easy to predict the position of all the possible emission lines. Almost all of them are effectively identified in the extremely congested high resolution emission spectrum. A number of them are fortuitously superimposed and therefore left over in the computation but enough lines are correctly measured so as to give rise to very satisfactory sets of constants ( $T_v$ ,  $B_v$ ,  $D_v$ ). At the present stage we have concentrated on the (unperturbed) Q-branches of the C, D, D', D''  $1\Pi_u \rightarrow X \ 1\Sigma_g^+$  transitions. Up to 500 lines of a transition are entered in the program which fits the constants of both the ground state and the excited states of symmetry  $1\Pi_u^-$ .

In a few branches some lines appearing as narrow doublets are in fact clearly reabsorbed lines. Most of them are assigned to transitions toward  $v'' = 0$  but some of them are ascribed to transitions toward  $v'' = 1$  thus indicating the presence of appreciable amount of H<sub>2</sub> ( $v'' = 1$ ) in our discharge like in the conventional discharge used by preceding workers<sup>3</sup>.

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Study of the Dissociation energy of BN molecule

\*

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ABSTRACT

The study of dissociation energy of Boron nitride molecule is a promising field, both experimentally and theoretically. The results of such studies are valuable to astrophysics, combustion phenomenon and astronomy. Known  $D_0$  values are inadequate and controversial. It is therefore the Rydberg-Klein-Rees (RKR) potential energy curves of the  $X^3 \Pi$  state and  $A^3 \Pi$  state of BN have been calculated using D<sub>0</sub>CK 1090 computer. The dissociation energy for the ground state of BN molecule has been estimated by the method of curve fitting using the three-parameter Lippincott potential function. The band strength of BN (A-X) systems are also studied using the Franck-Condon factors and percentoid values adopting the authors' method.

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+ L.S.Gowda and V.N.Balaji, *Spy. lett. (New York)* 10, 1 (1977)

## Predissociations in the B $^3\Pi_0^+$ state of ICl

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For the B  $^3\Pi_0^+$  state of ICl, only the  $v=0, \dots, 3$  levels have been observed. The  $v=3$  level (not yet observed in fluorescence) is perturbed by predissociation. It is generally believed that the B state dissociates into the ground state I ( $^2P_{3/2}$ ) plus an excited Cl ( $^2P_{1/2}$ ).

Using a very narrow cw dye ring laser, the absorption spectrum of ICl has been investigated in the region of  $17320\text{ cm}^{-1}$  to  $17650\text{ cm}^{-1}$  to study the  $3-1$  band of the B  $^3\Pi_0^+ \leftarrow X\ ^1\Sigma^+$  system and some fragmentary bands, which were attributed to the transition from an adiabatic B' state to the ground state X/1/.

The results of a very thorough analysis showed an oscillatory behaviour of predissociative linewidths and energy shifts in  $v=3$  as a function of the rotational quantum number J. This could be partly explained within the semi-classical model of Child /2/ as heterogeneous ( $\Delta\Omega=1$ ) predissociation caused by a weakly interacting state with  $\Omega=1$ . But there is also evidence for a contribution of homogeneous predissociation ( $\Delta\Omega=0$ ).

The additional analysis of the fragmentary bands from vibrational states above  $v=3$  leads to the final conclusion that there might exist 4 curve crossings not clearly separated from each other in energy and internuclear distance; in our model, the B  $^3\Pi_0^+$  state leads to I ( $^2P_{1/2}$ ) + Cl ( $^2P_{3/2}$ ), and is crossed by a repulsive (Z)1, a repulsive (Y)O<sup>+</sup> and a weakly bonding (Y')O<sup>+</sup> state. The avoided crossing of the latter O<sup>+</sup> states forms the adiabatic B'. The corresponding fragmentary bands can be discussed in the intermediate coupling scheme of Child and co-workers.

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- /2/ e. g. M. S. Child in Specialist Periodical Reports - Molecular Spectroscopy, Vol. 2, The Chemical Society London 1974

## The $r_s$ -structure of s-cis acrolein

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Recently, 25 years after the first report on the rotational spectra of s-trans acrolein [1], the microwave spectra of the s-cis conformer have been assigned [2].

As a continuation of [2], we have investigated the microwave spectra of  $^{18}\text{O}$ ,  $^{13}\text{C}$  and D substituted acrolein.

Comparison of the  $r_s$ -structures of the s-cis and s-trans conformers enables to discuss the effect of the conformation on the structural parameters for 1,3-conjugated systems.

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J.Chem.Phys., 26 (1957) 634.

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Chem.Phys.Lett., 88 (1982) 55.

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MICROWAVE SPECTRA OF 1,3,5-BORADIOXAZINE AND 1,3,5-BOROXADIAZINE

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In the previous study on the detection of  $\text{BH}_2\text{NH}_2$  by microwave spectroscopy, we found that this intermediate was produced in the reaction between diborane and nitrogen oxide as well as between diborane and ammonia. Furthermore, we found unexpected spectra in the reaction of diborane and nitrogen oxide, and were able to identify them to those of new molecules with boroxine type planar ring structures.

First, we found condensed bunch spectra at 31.0, 36.7, 42.3, and 48.0 GHz which consisted of characteristic Q-branch series by nearly symmetric rotor. Although the molecule was singled out at all, the rotational constants were determined to be  $A=5663.69(8)$  MHz,  $B=5616.51(5)$  MHz, and  $C=2820.411(14)$  MHz. In order to identify the origin of the spectra, the isotopically substituted species were measured by using  $\text{B}_2\text{D}_6$  and  $^{15}\text{NO}$ . From the rotational constants obtained, it was concluded that one of the new molecules produced in the reaction of diborane and nitrogen oxide was 1,3,5-boradioxazine. Also we found another new molecule in the same reaction and identified it to 1,3,5-boroxadiazine. The latter, however, showed weaker spectrum compared to the former.

The following experimental conditions were used for the observation of the spectra. The mixture of  $\text{B}_2\text{H}_6$  and  $\text{NO}$  with the ratio of 2 to 1 was heated in a quartz tube with 6mm in inner diameter and 30cm in length. The sample was continuously pumped through the microwave cell. The best spectra were obtained when the temperature of the quartz tube was around  $500^\circ\text{C}$  and the cell temperature was about  $-20^\circ\text{C}$ . The lifetimes of the new species were measured to be several minutes in the cell. However, it is not certain that they are essentially unstable compounds.

MICROWAVE SPECTRUM OF METHYL HYDROPEROXIDE ( $\text{CH}_3\text{OOH}$ ):

INTERNAL ROTATION EFFECTS OF METHYL AND HYDROXYL GROUP

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The microwave spectrum of methyl hydroperoxide has been investigated from 12.5 to 60 GHz. First, a series of strong high J Q-branch transitions with a linear Stark effect as well as some R-branch transitions were recognized. They had to be explained as  $\mu_c$ -type transitions between the lowest symmetric and antisymmetric states of the hydroxyl torsion. The energy difference between the two states was estimated to be around  $15 \text{ cm}^{-1}$ . Later weaker pure rotational  $\mu_a$ - and  $\mu_b$ -type R-branch transitions in the four lowest states of the hydroxyl torsion could be assigned with the help of microwave-microwave double resonance. A number of transitions were further split into a doublet due to the internal rotation of the methyl group.

In order to account for all the observed transitions an approximate Hamiltonian was introduced. It modeled the strong interaction between the two lowest states of the hydroxyl torsion with two Coriolis coupling terms and the energy difference. The rotational energies were described with individual rotational and centrifugal distortion constants for each state. These parameters were adjusted simultaneously to the measured transition frequencies. Consequences for the barriers to internal rotation of the methyl and hydroxyl group were deduced from comparison with a rigorous calculation of a non-rigid model of the internal rotations.

HYPERFINE AND ISOTOPLICALLY INVARIANT PARAMETERS  
OF THE  $\text{GeS}$  MICROWAVE SPECTRUM

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The complete set of microwave data for the 9 isotopic species of the  $\text{GeS}$  molecule, available in literature, is reduced to molecular parameters by a non-linear least squares fit. All the hfs lines due to  $^{73}\text{Ge}$  ( $I = 9/2$ ) and  $^{33}\text{S}$  ( $I = 3/2$ ) are included in this fit.

Watson's expressions of Dunham coefficients, including corrections to the Born-Oppenheimer approximation, are used. Contributions from off-diagonal terms are taken into account in the hfs Hamiltonian which is numerically diagonalized.

A set of 12 hyperfine and isotopically invariant parameters is obtained and compared with previous determinations. It is shown that the accuracy of the hfs parameters is improved by one order in magnitude by the global treatment of all the data.

PREPARATION AND MICROWAVE SPECTRUM OF THE  
NEW PHOSPHA-ALKENE  $\text{CH}_2=\text{PCN}$

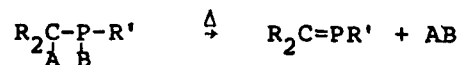
M.C. Durrant and H.W. Kroto

School of Molecular Sciences

University of Sussex Falmer Brighton BN1 9QJ

ABSTRACT

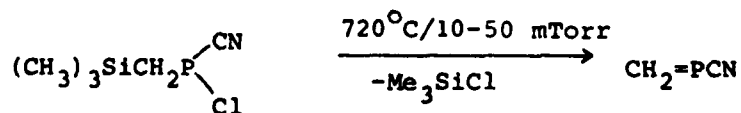
Phospha-alkenes can be produced by low pressure  
pyrolytic elimination from an appropriate precursor:



So far the choice for the molecule AB is limited to  
 $\text{HCl}$ ,  $\text{HF}$ ,  $\text{H}_2$ ,  $\text{CH}_4$ ,  $\text{Me}_3\text{SiH}$  and  $\text{Me}_3\text{SiCl}$ . Of these, the  
silanes are found to be the most efficient.

With this in mind, a synthesis for compound (1)  
has been developed; pyrolysis of this compound has  
yielded the new phospha-alkene  $\text{CH}_2=\text{PCN}$ .

The microwave spectrum of this molecule has been  
investigated.



(1)

SPECTRE DE VIBRATION-ROTATION DE LA MOLECULE D'ALLENE DANS LA REGION DE 730 A 1150  $\text{cm}^{-1}$   
DETERMINATION DES NIVEAUX D'ENERGIE ET DES CONSTANTES SPECTROSCOPIQUES ASSOCIEES AUX  
BANDES  $\nu_9$  ET  $\nu_{10}$

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-----  
Le spectre de vibration-rotation de la molécule d'allène ( $\text{H}_2\text{C}=\text{C}=\text{CH}_2$ ) dans la région de 730 à 1150  $\text{cm}^{-1}$  a été enregistré à l'aide du spectromètre à Transformée de Fourier du Laboratoire de Spectronomie Moléculaire à une résolution de 0,002  $\text{cm}^{-1}$

Environ 5000 raies appartenant aux bandes  $\nu_9$ ,  $\nu_{10}$  ont pu être attribuées et de nombreuses perturbations des niveaux d'énergie de ces deux bandes ont été mises en évidence ; en particulier une forte interaction de Coriolis de type 2 entre les bandes  $\nu_9$  et  $\nu_{10}$ .

Le calcul des constantes spectroscopiques a été mené à l'aide du système de programmes, conçu par J. Pliva, pour l'analyse des molécules à symétrie axiale en tenant compte des diverses perturbations dues aux bandes  $\nu_4$ ,  $2\nu_{11}$ ,  $\nu_3$  et  $3\nu_{11}$  présentes dans cette région.

Nous donnons les constantes spectroscopiques associées aux bandes  $\nu_9$  et  $\nu_{10}$ , les valeurs des constantes des deux dédoublements du type 2 ainsi que les valeurs de la constante d'interaction de Coriolis de type 2.



The Far Infrared Spectrum of HNCO.

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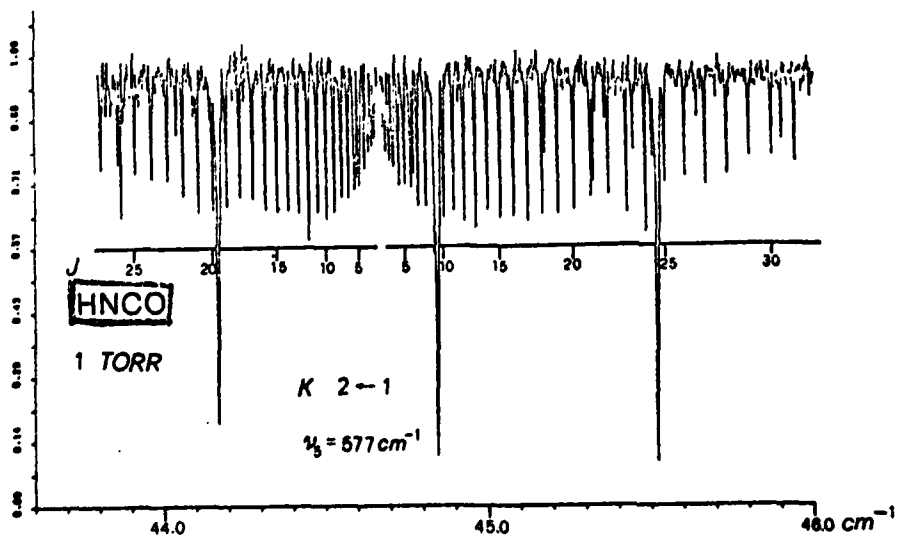
The far infrared spectrum of gaseous HNCO has been recorded  
between 8 and 80  $\text{cm}^{-1}$  with a resolution of about  $0.004 \text{ cm}^{-1}$ .

Pure rotational transitions in the ground vibrational state  
have been measured and assigned.

These are the a-type  ${}^qR_K$  transitions up to  $J = 60$  and the  
b-type  ${}^rP_0$ ,  ${}^rQ_0$ ,  ${}^rR_0$ ,  ${}^rP_1$  and  ${}^rR_1$  transitions.

In addition the  ${}^rQ_K$  pure rotational transitions in the exci-  
ted bending vibrational states have been identified:  ${}^rQ_0$  of  
 $\nu_4$  at  $51.33 \text{ cm}^{-1}$ ,  ${}^rQ_1$  of  $\nu_5$  at  $44.66 \text{ cm}^{-1}$ , and  ${}^rQ_0$  of  $\nu_6$  at  
about  $43.45 \text{ cm}^{-1}$ .

While the analysis of the ground state transitions is comple-  
ted, that of the excited states transitions is still in pro-  
gress.



## High Resolution Fourier and Laser Spectroscopy of Methanol

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CH<sub>3</sub>OH is the richest laser active molecular medium (more than 350 frequencies). The investigation of its spectrum is of great interest also because of theoretical reasons, since CH<sub>3</sub>OH is one of the simplest molecules displaying internal torsional rotation, accompanied by centrifugal distortions, Fermi interactions... , and because CH<sub>3</sub>OH has been observed in interstellar space. We are trying to get the most complete possible picture of the spectrum by combining FIR and IR Fourier absorption spectra with observed laser emissions and triple resonance experiments on the CH<sub>3</sub>OH laser.

The FIR spectrum, between 8 and 80 cm<sup>-1</sup>, has been recorded at the IROE laboratory, Italian CNR, in Florence, in collaboration with G. Bonetti, B. Carli and F. Mencaraglia of IROE, and of M. Carlotti, G. Di Lonardo and A. Trombetti of the University of Bologna. The resolution is 0.0033 cm<sup>-1</sup>, the peak precision 2x10<sup>-4</sup> cm<sup>-1</sup>. The vapour was contained in a 1.45 m long cell at a pressure of 1.98 Torr.

The IR spectrum, between 900 and 1100 cm<sup>-1</sup>, has been recorded on a BOMEM spectrometer at the Herzberg Institute of Astrophysics, NRC of Canada, in Ottawa, in collaboration with J.W.C. Johns. The peak precision is 5x10<sup>-2</sup> cm<sup>-1</sup>. The vapour was contained in a 15 cm long cell at a pressure of 1 Torr.

More than 1200 FIR and 600 IR lines have been assigned up to now. The line assignments have been performed by means of Taylor expansions of the energy levels sharing the same quantum numbers but J. In most cases an expansion in J(J+1) up to the third or fourth order is more than enough to match the experimental accuracy. Some v=1 states require an expansion in J rather than in J(J+1), this fact can be explained by the presence of some perturbation, like Fermi interactions. Experimental Taylor coefficients have been evaluated for all symmetries, v=0, v=1, K=0 to 10, n=0, and, in a few cases, n=1.

These FIR and IR measurements are combined with the CH<sub>3</sub>OH laser output frequencies and the results of triple resonance experiments on the CH<sub>3</sub>OH laser, so that complete loops of transitions are formed between two v=0 states and two or more v=1 states. The loop, providing a self-consistency check for all the assignments involved, is practically always a definitive test for the assignment of the laser line. This has helped us to solve some dubious assignments and also to find out some errors in the literature.

The  $2\nu_2$ ,  $\nu_1$  and  $\nu_3$  bands of  $\text{H}_2^{32}\text{S}$ ,  $\text{H}_2^{33}\text{S}$  and  $\text{H}_2^{34}\text{S}$

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The spectra of the  $2\nu_2$ ,  $\nu_1$  and  $\nu_3$  bands of the hydrogen sulfide have been recorded between 2150 and 2950  $\text{cm}^{-1}$  on a BOMEM Fourier transform spectrometer with a resolution of 0.005  $\text{cm}^{-1}$ .

The recent data concerning the (000) vibrational state obtained in the far infrared on the same instrument combined with a careful analysis of these spectra has enabled us to obtain a precise set of rotational levels of the three vibrational states (020), (100), (001) for the three isotopic species  $\text{H}_2^{32}\text{S}$ ,  $\text{H}_2^{33}\text{S}$ ,  $\text{H}_2^{34}\text{S}$  observed in natural abundance. These vibrorotational levels have been introduced in a least squares fit leading to the determination of rotational and coupling constants for the three interacting states and this for each isotope.

Finally individual line strengths measurements were performed and from them it has been possible to determine the expansion of the transformed transition moment operator of the three bands  $2\nu_2$ ,  $\nu_1$  and  $\nu_3$ .

$^{12}\text{C}^{16}\text{O}^{18}\text{O}$  - ANALYSIS OF EMISSION FOURIER SPECTRA IN THE 4.5  $\mu\text{m}$  REGION:  
ROVIBRATIONAL TRANSITIONS  $\text{OV}_2^{\ell}\text{V}_3 - \text{OV}_2^{\ell}(\text{V}_3-1)$ ,  $\text{V}_2 = \ell$ .

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In order to study the vibrational levels on the  $\text{CO}_2$  molecule and those of its main isotopic species, the emission spectra of  $\text{CO}_2\text{-N}_2$ ,  $\text{CO}_2\text{-He}$ ,  $\text{CO}_2\text{-N}_2\text{-He}$  gas mixtures excited by d.c. discharge have been recorded with a Fourier Transform Spectrometer between 1700 and 2400  $\text{cm}^{-1}$  (Resolving power :  $5.4 \cdot 10^{-3} \text{cm}^{-1}$ ).

The vibrational luminescence of 6 isotopic species  $^{12}\text{C}^{16}\text{O}_2$ ,  $^{12}\text{C}^{18}\text{O}_2$ ,  $^{13}\text{C}^{16}\text{O}_2$ ,  $^{13}\text{C}^{18}\text{O}_2$ ,  $^{12}\text{C}^{16}\text{O}^{18}\text{O}$ ,  $^{13}\text{C}^{16}\text{O}^{18}\text{O}$ , have been observed: for each one, thousands of lines from band sequences  $\Delta\nu_3=1$  have been assigned.

Results from symmetric molecules have been reported in previous papers. We shall present results obtained from the analysis of 15 vibrational transitions concerning the asymmetric species  $^{12}\text{C}^{16}\text{O}^{18}\text{O}$ .

We shall give the spectroscopic constants associated with the 33 vibrational levels or sublevels observed; these constants allow us to reproduce the experimental wavenumbers with a R.M.S. by transition  $< 8 \cdot 10^{-5} \text{cm}^{-1}$  in most cases, the best being  $2.7 \cdot 10^{-5} \text{cm}^{-1}$ . Molecular parameters have been determined from 4 transitions  $\Sigma \rightarrow \Sigma$ ; the validity of such parameters will be discuss in relation with previous results concerning symmetric molecules.

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THE SPECTRUM AND STRUCTURE OF CH<sub>2</sub> IN THE  $\tilde{X}^3B_1$  STATE AND THE ACCURATE  
DETERMINATION OF THE SINGLET-TRIPLET SPLITTING

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During the last two years much infrared and far infrared spectra of gas phase CH<sub>2</sub> in its  $\tilde{X}^3B_1$  electronic ground state have been analysed. For <sup>12</sup>CH<sub>2</sub> Laser Magnetic Resonance has been used to study the  $\nu_2$  (bending) band and the pure rotation spectrum (1-3). LMR spectra of the  $\nu_2$  band of <sup>13</sup>CH<sub>2</sub> (4), far infrared LMR of CD<sub>2</sub> (5), and diode laser spectra of the  $\nu_2$  band of CD<sub>2</sub> (6) have also been obtained. Using the nonrigid bender Hamiltonian this data has been analysed to yield the equilibrium structure and potential function for the triplet state (7,8).

Very recently we have assigned some far infrared LMR spectra to transitions involving  $\tilde{a}^1A_1$  excited electronic state energy levels perturbed by rotation-vibration levels of the  $\tilde{X}^3B_1$  state. Analysis of these perturbations leads to a determination of  $T_0(\tilde{a}^1A_1) = 3170 \text{ cm}^{-1}$ .

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ETUDE DU SPECTRE INFRAROUGE DU SILANE DANS LA REGION DE 2 050 A  
2 300  $\text{cm}^{-1}$ . ANALYSE DES NIVEAUX  $\nu_1 = 1$  et  $\nu_3 = 1$ .

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Le spectre infrarouge des bandes  $\nu_1$  et  $\nu_3$  du Silane enregistré sur le spectromètre à transformée de Fourier du Laboratoire d'Infrarouge d'Orsay a été analysé. L'Hamiltonien de CHAMPION a été développé au 4ième ordre d'approximation aussi bien pour les termes diagonaux en  $\nu$  que pour les termes d'interactions entre les états  $\nu_1 = 1$  et  $\nu_3 = 1$ .

Pour l'analyse de la diade  $\nu_1$  et  $\nu_3$  du  $^{28}\text{SiH}_4$ , nous avons utilisé plus de 500 niveaux déterminés à partir de plus de 1 800 transitions expérimentales infrarouges et les 3 transitions microondes de TAKAMI obtenues par double résonance. Notre analyse est pondérée par des poids liés à la précision des données expérimentales. Nous reproduisons les niveaux d'énergie de  $\nu_1$  et  $\nu_3$  déduits des données infrarouges avec un écart type non pondéré inférieur à 2 mK, et nous reproduisons également les 3 transitions microondes avec un écart type non pondéré de 0,4 MHz soit de  $1.2 \times 10^{-5} \text{ cm}^{-1}$ .

Nous pensons développer cette technique et introduire toutes les données disponibles par exemple Raman et CARS.

Une analyse des deux autres espèces isotopiques  $^{29}\text{SiH}_4$  et  $^{30}\text{SiH}_4$  a été réalisée. La qualité des résultats est comparable à celle obtenue pour  $^{28}\text{SiH}_4$ .

J

LINE STRENGTHS ANALYSIS :  $\nu_2$  AND  $\nu_4$  BANDS OF  $^{12}\text{CH}_4$ .

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Using a tensorial formalism in the  $I_d$  group, we have determined all the vibration-rotation operators of the dipole moment of  $\text{XY}_4$  molecules, up to any order of approximation [1]. This general formalism is available for any transition between vibrational sublevels of any symmetry. It can be used for the analysis of isolated bands and for the analysis of interacting bands as well. The theory is applied to the analysis of rovibrational line strengths of the two bands  $\nu_2$  and  $\nu_4$  of  $^{12}\text{CH}_4$  alone and as a polyad, on the basis of a first or a second order expansion of the dipole moment.

Five operators are needed to analyse the strengths of the isolated  $\nu_4$  band. It is shown that the empirical Hermann-Wallis polynomial is not adapted to this problem, especially in the case of the "forbidden" lines. The I.R "forbidden"  $\nu_2$  band has been analysed as an isolated band with two operators.

As pointed out by many authors, the best model for these two interacting bands is the dyad scheme. On this basis, we have also analysed the line strengths with the adapted first order expansion of the dipole moment. To this order, we have three operators. The corresponding parameters are found to be :

$$\begin{aligned} \mu_4(0, A_1) &= .09870 \quad (18) \quad \text{Debye} \\ \mu_4(1, F_1) &= - .289 \quad (14) \quad 10^{-3} \quad - \\ \mu_2(1, F_1) &= - .226 \quad (16) \quad 10^{-3} \quad - \end{aligned}$$

The obtained parameters are compared to their theoretical value and their physical meaning is also discussed. It is shown that the usual correction factor  $F$  depends on all quantum numbers and has a tetrahedral structure.

In addition, we present preliminary results on the  $\nu_2 + \nu_3$  band. With two vibrational sublevels ( $F_2$  and  $F_1$ ), this band has the same kind of behaviour as the dyad.

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INTERFERENCE EFFECTS IN THE INFRARED SPECTRUM OF HD  
AT HIGH PRESSURE

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At elevated pressures, the  $v = 1 + 0$  fundamental band of HD consists of two parts: (1) a broad collision-induced quasi-continuum arising from dipoles induced during molecular collisions, and (2) a dipole-allowed part with sharp lines arising from the small permanent dipole moment of the isolated HD molecule. A number of previous experimental<sup>1-3</sup> and theoretical<sup>3-6</sup> studies have shown that interesting interference effects occur between these two components.

We have extended this work by studying the 1-0 band at 77 °K with pressures in the range 5 to 40 atmospheres using a Bomem spectrometer in the 2.7  $\mu\text{m}$  region. With increasing pressure, the sharp R(0) and R(1) dipole lines lose intensity and become increasingly asymmetric. Each transition can be well fitted by a series of Fano line profiles, similar to those arising in autoionized atomic spectra. However, the behaviours of R(0) and R(1) are quite different from each other. The pressure variation of the shapes and intensities can be accounted for using the approach of Herman, Tipping and Poll<sup>6</sup> but this theory has not yet been sufficiently developed to predict the values of the phase shift parameters which are obtained in the analysis.

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SPECTRAL INTENSITIES IN THE  $\nu_5$  BAND OF  $^{12}\text{CD}_3\text{H}$

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The absolute intensities of 68 transitions belonging to the  $\nu_5$  band of  $^{12}\text{CD}_3\text{H}$  have been measured in the range 1237.8 - 1362.4  $\text{cm}^{-1}$  using tunable diode lasers. The absorption spectra recorded at Doppler limited resolution have allowed to derive the data from the peak absorption coefficients with the only correction for residual pressure broadening. A self-broadening coefficient measured equal to  $0.067 \pm 0.007 \text{ cm}^{-1} \text{ atm}^{-1}$  has been used.

The absolute intensities have been measured at  $296 \pm 1 \text{ K}$  and the values corrected for the abundance (97.8 percent) of  $^{12}\text{CD}_3\text{H}$  in the gas sample. A minimum set of four different sample pressures have been measured for each transition. The quoted relative uncertainties result mainly from the statistical dispersion of the measured data.

The experimental material has been used to derive the intensity parameters for the  $\nu_5$  band. The line strengths are calculated on the basis of the transformed dipole moment  $\mu_z^t$  expanded to quadratic terms in  $P_\alpha$  (components of angular momentum). Assignments of the lines, as well as eigenfunctions required for transition moment calculations are derived according to the up to date frequency results given in References (1-3).

The fit of the experimental data has led to three significant parameters, including the vibrational moment  $\langle \mu_z \rangle$  and the two corrections linear in J and K involved in the expansion of the transition moment  $\langle |\mu_z^t| \rangle$ . With these three parameters, the 68 line strengths are reproduced with an average relative uncertainty equal to 2.3 percent, compared to 2.5 percent for the experimental one. The results will be presented with more details in the poster.

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ROTATIONAL ANALYSIS OF THE  $\nu_2 + \nu_4^{\pm 1}$ ,  $\nu_2 + 3\nu_6^{\pm 1}$ ,  $\nu_4 + \nu_5^{\pm 1}$ ,  $\nu_4 + \nu_5^{\pm 1}$ ,  $\nu_5 + 3\nu_6^{\pm 1}$ ,  
 $\nu_5^{\pm 1} + 3\nu_6^{\pm 1}$ ,  $2\nu_3 + 3\nu_6^{\pm 1}$ ,  $\nu_1 + \nu_2$  AND  $\nu_1 + \nu_5^{\pm 1}$  INTERACTING INFRARED BANDS  
 OF METHYL CHLORIDE.

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$\nu_2 + \nu_4^{\pm 1}$  and  $\nu_4 + \nu_5^{\pm 1}$  are two strong perpendicular bands which lie  
 between 4250 and 4570  $\text{cm}^{-1}$ . We are studying them on a recording obtained by Dr. Guelachvili  
 on his Fourier transform interferometer with a resolution of 0.0075  $\text{cm}^{-1}$  ( $p \sim 0.8$  torr,  
 $l = 28$  meters).

The assignment of the lines is quite difficult because of the great  
 number of perturbations, generally caused either by the Coriolis resonance between the  $\nu_2$   
 and  $\nu_5$  modes, or by the Darling-Dennison resonance between  $\nu_4^{\pm 1}$  and  $3\nu_6^{\pm 1}$ . At the  
 present time more than 2500 lines, all belonging to the  $\text{CH}_3^{35}\text{Cl}$  species, have been assigned;  
 the Coriolis resonance between  $\nu_2 + \nu_4^{\pm 1}$  and  $\nu_4 + \nu_5^{\pm 1}$  is of course quite visible with  
 forbidden lines at the crossing of the levels; but we still need to find several  $K'$  sub bands  
 which would be very useful for the modeling:  $\nu_2 + \nu_4^{\pm 1}$  and  $\nu_4 + \nu_5^{\pm 1}$  indeed are coupled  
 to many other bands which are too weak to be normally observed, and we can only obtain  
 the necessary informations through searching for the level crossings. We have thus already  
 observed the crossing of  $\nu_2 + 3\nu_6^{\pm 1}$  with  $\nu_2 + \nu_4^{\pm 1}$  (1), and then the crossing of  $\nu_5^{\pm 1} + 3\nu_6^{\pm 1}$   
 with  $\nu_4^{\pm 1} + \nu_5^{\pm 1}$ ; the latter is complicated because three  $K' \cdot \Delta K = -2$  sub bands are visible,  
 the third one being very likely caused by  $2\nu_3 + 3\nu_6^{\pm 1}$  which is linked to  $\nu_5^{\pm 1} + 3\nu_6^{\pm 1}$  by  
 an anharmonic coupling (2).

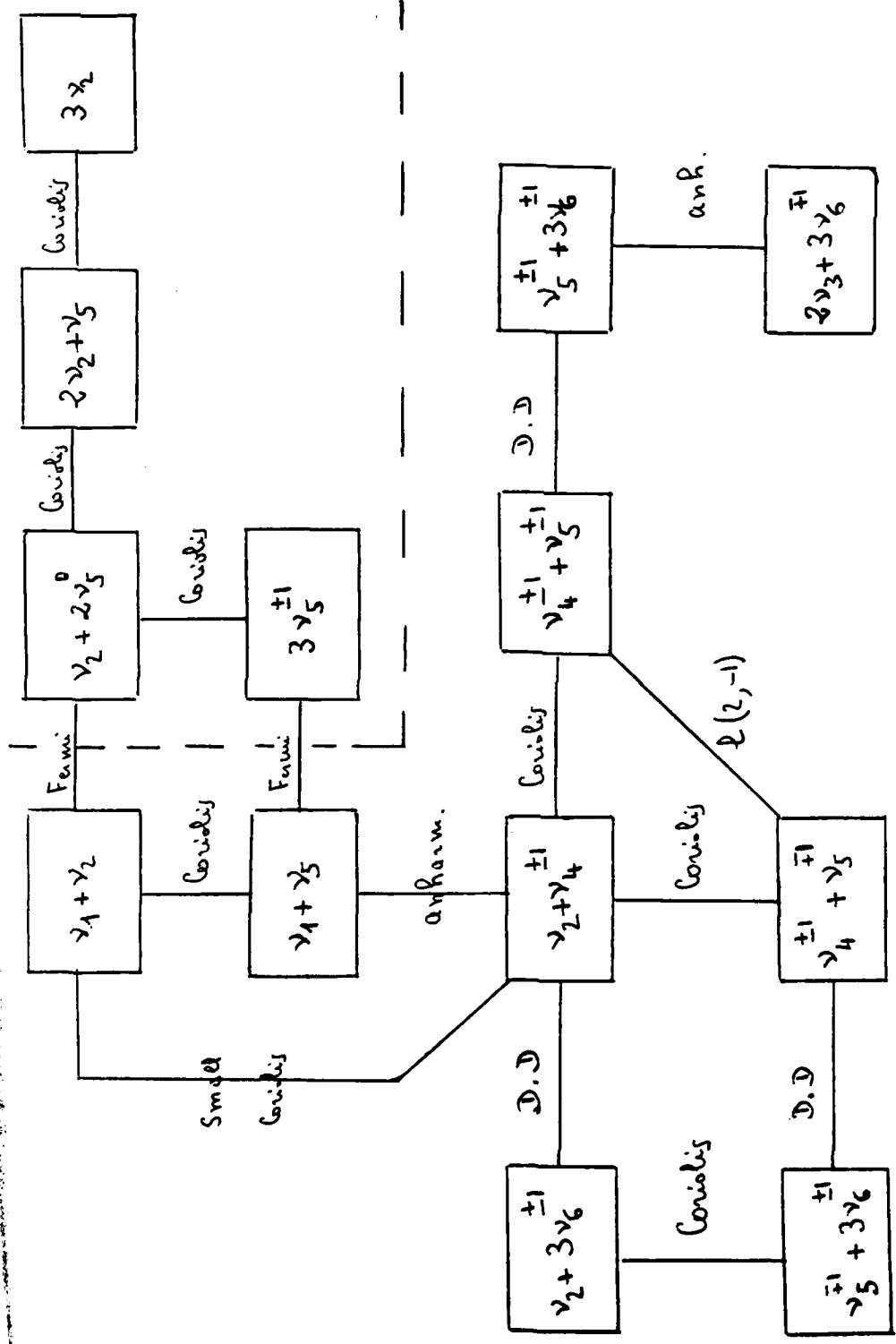
The  $\Delta K = -1$  side of  $\nu_2 + \nu_4^{\pm 1}$ , already crossed by  $\nu_2 + 3\nu_6^{\pm 1}$   
 (for  $K' \sim 1$ ) and by  $\nu_4^{\pm 1} + \nu_5^{\pm 1}$  (for  $K' = 8$ ), shows at least two supplementary perturba-  
 tions: the  $K' \cdot \Delta K = -6$  sub band is double because of a crossing with  $\nu_1 + \nu_2$  (3), and  
 there is very likely an anharmonic resonance between  $\nu_2 + \nu_4^{\pm 1}$  and  $\nu_1 + \nu_5^{\pm 1}$ , with a  
 crossing of levels at  $K' \sim 8$  giving rise to two  $P_Q$  branches of  $\nu_1 + \nu_5$  by energy  
 transfer from  $\nu_2 + \nu_4$ . Of course  $\nu_1 + \nu_5$  and  $\nu_1 + \nu_2$  are coupled by Coriolis resonance  
 and should involve  $\nu_2 + 2\nu_5^0$ ,  $2\nu_2 + \nu_5$ ,  $3\nu_2$  and  $3\nu_5^{\pm 1}$  through the Fermi  
 resonance between  $\nu_2$  and  $2\nu_5^0$  (3), but we hope to be able to avoid taking these  
 bands into account.

As for the  $\nu_4^{\pm 1} + \nu_5^{\pm 1}$  parallel band, we have not yet observed any  
 of its lines, but we would like to find a few of them either at its crossing with  $\nu_2 + \nu_4$   
 (expected for  $K' \cdot \Delta K = +7$ ) or with  $\nu_4^{\pm 1} + \nu_5^{\pm 1}$  to which it is linked by a  $l(2, -1)$   
 resonance whose effects are quite visible on the  $R_{Q_0}$  branch of  $\nu_4^{\pm 1} + \nu_5^{\pm 1}$ .

(1) Ben Sari-Zizi, Alamiichel and Guelachvili (J. Phys. Paris 42, 627-34, 1981)

(2) El Loure and Alamiichel (J. Mol. Spectrosc. 81, 390-412, 1980)

(3) Ben Sari-Zizi and Alamiichel (Helv. Phys. 43, 1255-65, 1981)



Ben San Alam, lhd

LEAST SQUARES DETERMINATION OF THE TRANSITION DIPOLE MATRIX  
ELEMENTS FOR  $^{14}\text{NH}_3$  FROM THE LINE INTENSITIES OF THE  
 $2\nu_2$  AND  $\nu_4$  BANDS

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Line intensities as well as self and nitrogen broadening coefficients have been determined for 20 transitions in the  $2\nu_2$  and  $\nu_4$  bands of  $^{14}\text{NH}_3$  using a diode laser spectrometer. Vibrational transition moments have been determined for the transitions from the ground state to the  $\nu_2$ ,  $2\nu_2$ , and  $\nu_4$  states by a least squares fit to the line intensities taking into account Coriolis and  $\ell$ -type interactions between the  $n\nu_2$  ( $n=1,2,3$ ),  $\nu_4$ , and  $\nu_2 + \nu_4$  states (Š. Urban et al., J.Mol.Spectrosc. 79, 455-495 (1980)). This has made it possible to quantitatively describe drastic perturbations of line intensities in both the  $2\nu_2$  and  $\nu_4$  bands. The analysis leads also to a unique determination of the sign relationship between the dipole moment derivatives and the vibrational angular momentum resulting from the interaction between the inversion motion and the  $\nu_4$  doubly degenerate vibrational mode.

Spectres vibration-rotation de la molécule DCP. Enregistrement dans la région de la fondamentale  $\nu_2$ , interprétation du spectre et calcul des constantes spectroscopiques des états  $01^10$ ,  $02^00$  et  $02^20$ .

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Le spectre vibration-rotation de la molécule  $D^{12}C\equiv P$  a été enregistré dans la région spectrale comprise entre 575 et 475 nombre d'ondes utilisant un interféromètre BOMEM procurant une résolution de  $4 \times 10^{-3}$  nombre d'onde. Le spectre a été enregistré dans le laboratoire du Dr J.W.C Johns à l'Institut d'Astrophysique Herzberg d'Ottawa. Depuis ce temps notre laboratoire a acquis un appareil identique. La fondamentale  $\nu_2$  se trouve centrée sur cette région; les transitions ont été identifiées jusqu'à R(42), P(44) et Q(52). Outre  $\nu_2$ , cette région contient aussi les bandes chaudes correspondant aux transitions de l'état  $01^10$  à l'état  $02^00$  et l'état  $02^20$ . Au total, 360 transitions impliquant les états  $00^00$ ,  $01^10$ ,  $02^00$  et  $02^20$  ont été utilisées pour obtenir, par un calcul simultané, les constantes spectroscopiques de ces états (15 au total) incluant les constantes  $q$  et  $u$  des états  $\nu_2=1$  et  $\nu_2=2$ . Le résidu moyen sur les 360 transitions est de  $2.2 \times 10^{-4} \text{ cm}^{-1}$ .

Mai 1983.

PARAMETRES D'ELARGISSEMENT PAR LA PRESSION DE RAIES DE VIBRATION-ROTATION (BANDE  $\nu_3$   
DE  $N_2O$  ET BANDES FONDAMENTALES DE CO et de HBr)

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Le spectromètre à réseau du laboratoire a été utilisé pour la mesure des paramètres d'élargissement par la pression des raies de vibration-rotation d'un certain nombre de bandes de vibration-rotation. Les systèmes suivants ont été étudiés :

- Le protoxyde d'azote (bande  $\nu_3$ ) avec l'azote ou l'oxygène ;
- L'oxyde de carbone (bande 1-0) avec l'azote ou l'hydrogène ;
- Le bromure d'hydrogène (bande 1-0) avec lui-même ou avec le dioxyde de carbone.

Les mesures ont été effectuées à la température ambiante et, pour  $N_2O$  et CO, à la température de 195 K.

Les résultats expérimentaux sont confrontés à des calculs effectués en utilisant divers modèles théoriques. La théorie Anderson-Tsao-Curnutte a été appliquée pour l'ensemble des molécules considérées. Dans le cas des systèmes  $N_2O-N_2$  et  $N_2O-O_2$ , la théorie Robert Bonamy a également été utilisée (en collaboration avec N. Lacôme, Laboratoire d'Infrarouge - Université de Paris Sud - Orsay).

Pour la molécule HBr, on a d'autre part déterminé les intensités des raies de la bande fondamentale en même temps que les paramètres d'auto-élargissement par la pression.

Rotational Spectra of  $^{15}\text{N}$ -labeled Diazirine Isotopomers,  $\text{H}_2\text{C}$  

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In the context of the investigation of the high resolution rotational rovibrational spectra of diazirine and some of its labeled isotopomers which are performed in our laboratory in Giessen we have measured the a-type-rotational spectra of the isotopically enriched isotopomers  $\text{H}_2^{12}\text{C}^{15}\text{N}_2$  and  $\text{H}_2^{12}\text{C}^{14}\text{N}^{15}\text{N}$  in the microwave and millimeter wave region from 8 to 300 GHz. The isotopomer  $\text{H}_2^{12}\text{C}^{15}\text{N}_2$  has been observed for the first time. Rotational and firstly centrifugal distortion constants have been determined for these isotopomers in the ground vibrational state.



**The Microwave Spectrum of Nitromethane and D<sub>3</sub>-Nitromethane  
Present Situation.**

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For nitromethane the barrier to internal rotation is very low,  $\sim 60$  GHz. This means that there are appreciable couplings between the different  $m$ -states (excited in the internal rotation quantum number  $m$ ), and consequently a spectral analysis must be carried out as a combined fit including all the states.

The spectrum is very rich and therefore there are many pitfalls in such an analysis. False assignments may easily slip by, especially since the number of necessary parameters invariably increases drastically with increasing  $J$  and  $m$ .

An estimate of the orders of magnitude shows that 28 parameters must be considered for lines with  $J$  up to 10 and  $m$  up to 3. For the two species about 60 lines could be fitted to 20 of these parameters. Thus the main features of the spectrum are well understood, but, the large number of high- $J$  and high- $m$  lines not accounted for in this type of analysis may raise doubt as to the assignments.

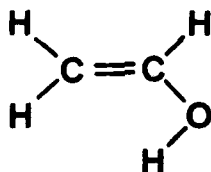
By a careful bootstrap procedure more lines has been included, at an expense of a small number of parameters, however: 19 sextic centrifugal distortion constants had to be considered as well as  $V_{12}$ . On the other hand it has been possible to fit many lines which are very accurately measured on the Fourier spectrometer of the University in Kiel (by the kind assistance of Prof. Dreizler and Dr. Fliege). For D<sub>3</sub>-Nitromethane two possible values of  $V_{12}$  have been found, 29.8 or 428 MHz.

MICROWAVE SPECTRUM, SUBSTITUTION STRUCTURE AND  
NORMAL COORDINATE ANALYSIS OF *syn*-VINYLALCOHOL

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The microwave spectra of *syn*-vinylalcohol



and nine isotopically substituted species have been investigated between 12.4 and 40 GHz. Rotational transitions of the vibrational ground state have been assigned up to  $J = 25$ . Rotational constants and all quartic centrifugal distortion constants have been adjusted from the measured transition frequencies. The substitution structure has been determined from the moments of inertia of seven singly substituted isotopic species. The data of two multi-deuterated species helped in confirming the sign of the coordinate of one hydrogen nucleus which lies near a principal axis.

In addition, the infrared spectra of ten isotopic species of vinylalcohol isolated in an argon matrix have been recorded and a normal coordinate analysis has been performed.

"ACOUSTIC DETECTION OF MM-WAVE PRESSURE BROADENING"

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P. MINGUZZI, M. TONELLI - Dipartimento di Fisica - Pisa - Italy

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We describe a novel experimental apparatus to measure the collision broadening of rotational lines in the millimeter-wave region. The sample cell is a small acoustic detector featuring high sensitivity at low pressure. The application of the photoacoustic technique to the millimeter-wave spectroscopy is rather uncommon (1,2) and only in few cases the results are comparable or superior to those obtained in conventional spectrometers. The main advantages of this new approach is the absence of standing waves which are often a difficult problem in lineshape spectroscopy. Another important feature of the apparatus is the very small dimension of cell which allows a tight control of the gas parameters such as purity, pressure and temperature.

We measured the broadening coefficients for  $\text{CH}_3\text{CN}$  and  $\text{CH}_3^{81}\text{Br}$  and compared them with the theoretically estimated linewidth.

- (1) A.F. KRUPNOV in "Modern Aspect of Microwave Spectroscopy"  
G.W. Chantry ed. Academic Press (London 1979)
- (2) G.BUFFA, A. DI LIETO, P. MINGUZZI, M. TONELLI:  
Int. J. of Infrared and Millim. Waves 2 (1981) 559.

ROTATION SPECTRA OF EXCITED VIBRATION STATES BY DRM MICROWAVE  
SPECTROSCOPY

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A comparison of the natural abundance of isotopes with the population of excited vibration states indicates (1) that substances, for which the rotation spectra of naturally occurring  $^{13}\text{C}$ -,  $^{15}\text{N}$ -,  $^{18}\text{O}$ - or D-forms can be observed at room temperature, should also allow the identification of the rotation spectra of all excited vibration states up to energies of  $\sim 1000\text{ cm}^{-1}$ ,  $\sim 1200\text{ cm}^{-1}$ ,  $\sim 1300\text{ cm}^{-1}$  or  $\sim 1800\text{ cm}^{-1}$ , respectively. We have tested this idea on furazan (1,2,5-oxadiazole,  $\text{C}_2\text{H}_2\text{N}_2\text{O}$ ,  $\mu = \mu_b = 3.38\text{ D}$ ) and a study of trifluoroethylene (trifluoroethene,  $\text{CF}_2=\text{CFH}$ ,  $\mu = \mu_b = 1.32\text{ D}$ ) is in progress.

- a) Furazan - Excited state spectra were identified up to  $1640\text{ cm}^{-1}$ , including 12 of the 15 fundamental levels. Strong Coriolis coupling occurs between  $\nu_{13}$  and  $\nu_{14}$ , and smaller perturbations are noted in several other satellites. Correlation of rotational satellites with vibrational levels (2) was based on the symmetry and population of states. The assignments of  $\nu_{12}$  and  $\nu_5$  was confirmed by laser/MW double resonance (Universität Ulm). The 12 fundamentals were also identified in the perdeutero compound where the  $\nu_{13}/\nu_{14}$  coupling is removed.
- b) Trifluoroethylene - Mainly due to the presence of two low vibrations (3), there occur 63 vibrational levels in the energy range up to  $1300\text{ cm}^{-1}$ . To date, 55 rotational satellite spectra have been assigned and 44 of those have been interpreted in terms of the six lowest fundamentals, their overtone and combination levels.

1. O.L. Stiefvater, *J. Chem. Phys.* **63**, 2569 (1975)
2. D.H. Christensen, P.W. Jensen, J.T. Nielsen and O.F. Nielsen, *Spectrochim. Acta*, **29A**, 1393 (1973)
3. D.E. Mann, N. Acquista and E.K. Plyler, *J. Chem. Phys.* **22**, 1586 (1954)

Emission Spectra of CN in the UV and VUV Regions.

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The spectra previously investigated by Douglas and Routly<sup>1</sup> and by Carroll<sup>2</sup> have been rephotographed in the 4th to 7th orders of the 10m vacuum spectrograph. The light source, a radiofrequency discharge through streaming pure HCN, produced spectra that were virtually free of overlapping CO bands. The spectra were examined from approximately 1700 to 3200 Å, and several new transitions were observed, the most interesting ones originating in three previously unidentified  $^2\Pi$  vibronic levels that provide clear evidence for a strong homogeneous perturbation of the higher  $D^2\Pi$  levels by a more strongly bound  $^2\Pi$  state. The new observations seem to confirm the results of ab initio calculations<sup>3</sup> that predict the existence of no more than three  $^2\Pi$  electronic states, including  $A^2\Pi$ , at energies of less than 8 eV.

<sup>1</sup>A.E. Douglas and P.M. Routly, *Astrophys. J. Suppl. Ser.* 1(9), 295-318 (1955)

<sup>2</sup>P.K. Carroll, *Can. J. Phys.* 34, 83-95 (1956)

<sup>3</sup>H.F. Schaefer and T.G. Heil, *J. Chem. Phys.* 54, 2573-2580 (1971)

THE A  $^1\Pi$  - X  $^1\Sigma^+$  TRANSITION OF BCl

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Twenty two bands of the A  $^1\Pi$  - X  $^1\Sigma^+$  transition of BCl have been rotationally analysed. These analysis yielded precise constants for levels ranging from  $v = 0$  to  $v = 9$  in the ground state and from  $v = 0$  to  $v = 8$  in the excited state.

The derived equilibrium constants are given below.

Equilibrium constants ( $\text{cm}^{-1}$ )

	X $^1\Sigma^+$	A $^1\Pi$
$v_e$	0	36750.24
$\omega_e$	840.01(14)	852.25(59)
$\omega_e x_e$	5.426(38)	12.91(26)
$\omega_e y_e$	0.0253(25)	0.160(41)
$\omega_e z_e$	-	0.0418(22)
$B_e$	0.684392(73)	0.70790(49)
$\alpha_e$	0.006764(47)	0.01082(57)
$\gamma_e$	0.0000277(33)	0.00033(14)
$\delta_e$	-	0.000076(11)
$(10^6)D_e$	1.919(13)	1.86(16)
$(10^6)\beta_e$	-	0.236(32)

NEW EMISSION BANDS IN THE HIGH RESOLUTION EMISSION SPECTRUM

OF N<sub>2</sub> BETWEEN 85 AND 90 nm

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As in the case of H<sub>2</sub><sup>1</sup>, the use of a low pressure discharge lamp allows us to prevent reabsorption at short wavelengths, leading to the preliminary observation of five new emission bands, namely c<sub>3</sub>'  $\Sigma_u^+$  → X  $\Sigma_g^+$  (v'=6, v'' = 0, 1, 2) and b'  $\Sigma_u^+$  → X  $\Sigma_u^+$  (v'=19, v''=1, 2)<sup>2</sup>.

Anomalies in intensity alternation in the P branch of the c<sub>3</sub>' → X(6, v'') bands may be due to configuration mixing of c<sub>3</sub>'  $\Sigma_u^+$  with other  $\Sigma_u^+$  and  $\Pi_u$  states. However the sudden breaking off of the P branch at J = 13 could be ascribed to a predissociation mechanism although configuration mixing cannot be totally ruled out as discussed by Yoshino for c<sub>3</sub>' (v'=1-4)<sup>3</sup>. In case of predissociation the limit should take place at an energy between those of the J' = 12 and 13 levels, namely at 117105.8 ± 22.8 cm<sup>-1</sup>, a value close to the known value 117160 ± 40 cm<sup>-1</sup> of the dissociation limit into 2D + 2D.

A reinvestigation of the entire emission spectrum is under way at a dispersion five times larger than before<sup>4</sup>.

- 1 - See communication about H<sub>2</sub> at the present Conference.
- 2 - c<sub>3</sub>' is named c<sub>4</sub>' in the literature but has been recently renamed by K. Dressler (private communication).
- 3 - K. Yoshino, D.E. Freeman and Y. Tanaka, J. Mol. Spectrosc. 76, 153 (1979).
- 4 - S.G. Tilford and P.G. Wilkinson, J. Mol. Spectrosc. 12, 231 (1969)





EVIDENCE OF A STRONG HYPERFINE u-g COUPLING NEAR THE DISSOCIATION LIMIT OF THE B STATE OF I<sub>2</sub>

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In the iodine molecule, Danyluk and King have observed five absorption bands between high vibrational levels of the  $B^3\Pi_0^+$  state and the first lowest ionic states. Only three of these ionic states ( $0^+g$ ,  $1g$ ,  $2g$ ) are to date identified. As it was noted in reference [1], the two other absorption bands ( $\gamma, \delta$ ) can only be connected to ionic "u" states. This means that the B state is mixed with a "g" state. Other experimental data [2,3] show that the hyperfine scalar spin-spin coupling parameter in the B state is positive; this fact emphasizes this hypothesis. Among all the terms of the interaction hamiltonian, only the hyperfine one allows a u-g coupling, as it is non-invariant through the inversion center (i) of the electronic point group  $D_{\infty h}$ . Another asymmetry comes from the eigenfunctions. The inversion symmetry is broken since the Heitler-London overlap integral is close to zero near the dissociation limit. We have extended our previous investigations [4] up to the B state dissociation limit. For vibrational levels  $v' < 75$  and  $v' \geq 79$  the hyperfine splittings can be accounted for with the help of four constants: electric quadrupole ( $eQq'$ ), magnetic dipole ( $c'$ ), scalar spin-spin coupling ( $\delta'$ ) and tensor spin-spin coupling ( $d'$ ). The variation of these constants as  $v'$  increases reflects the perturbation of the B state by several of the nine other electronic states sharing with B the same dissociation limit and can be accounted for by a second order perturbation theory. For  $v' = 76$  ( $J > 15$ ), 77, 78 the perturbation is so strong that a direct diagonalization of the interaction matrix is needed. The perturbing state is one of these nine electronic states. The matrix element calculation on the separated atoms basis shows that essentially the magnetic-dipole hamiltonian can strongly couple four states ( $0_u, 1u, 0_g, 1g$ ) to the B state. On the other hand, from the available ab-initio potential curves of these states [5], we have obtained, by a semi classical calculation, a significant vibrational overlapping with B only for the  $1g$  state. The direct diagonalization of the coupled system ( $Bu, 1g$ ) allowed us to interpret completely the observed perturbed hyperfine structures. An important result is that the magnetism introduced in the B state by the  $1g$  state is such that the nuclear spin I becomes a good quantum number. The identification of this ( $Bu, 1g$ ) coupling, purely hyperfine in origin, is the first definitive evidence for a long suspected u-g coupling in homonuclear molecules, never observed to date.

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- [4] J.P. Pique, F. Hartmann, R. Bacis and S. Churassy, Opt. Commun. 36, 354 (1981)
- [5] M. Saute and M. Aubert-Frécon, J. Chem. Phys. 77, 5639 (1982).

## Polarization Spectroscopy of Strontium Monohalide Radicals

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Strontium monohalide radicals are produced in a low pressure flame reaction of Sr and a halogen donor. Doppler free polarization spectroscopy offers the best sensitivity to study these species at high resolution /1/ and was used to observe sub-Doppler spectra of SrF and SrCl around 580 nm and 635 nm respectively. Several hundred lines from different vibrational bands of the  $B^2\Sigma^+ - X^2\Sigma^+$  systems could be assigned. The identification of the dense spectra was simplified by using microwave modulated polarization spectroscopy (MMPS), a combination of Doppler free polarization spectroscopy with microwave-optical polarization spectroscopy (MOPS)/2/. With this method rotational transitions of the ground state are induced by microwaves in order to label particular lines in the optical spectrum, necessary specially in the case of SrCl for which no reliable optical analysis existed.

The optical data were combined with the results of separate microwave measurements of the  $X^2\Sigma^+$  state in a weighted least-squares fit. This way the accuracy of spectroscopic constants of the  $B^2\Sigma^+$  state could be remarkably improved by the reduction of correlations between upper- and lower-state parameters.

/1/ W.E. Ernst, Opt.Comm. 44, 159 (1983)

/2/ W.E. Ernst and T. Törring, Phys.Rev.A 27, 875 (1983)

LASER STARK SPECTROSCOPY IN PROPYNE : THE  $\nu_5$  PARALLEL BAND

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The  $\nu_5$  parallel band of propyne,  $\text{CH}_3\text{C}_2\text{H}$ , has been studied, in the  $10 \mu$  spectral range, using :

- conventional high resolution spectroscopy with a SISAM interferometer (limit of resolution  $0.012 \text{ cm}^{-1}$ )
- laser Stark Spectroscopy using lines of  $^{13}\text{CO}_2$  and  $^{13}\text{CO}_2$  infrared laser, with electric field up to  $85 \text{ kV/cm}$ .

The zero field position of the lines allowed unambiguous predictions of the Stark coincidences using diagonalization matrix (11 x 11).

The Stark results had a high accuracy due to the observation of lambda-dip coincidences giving a resolution of about  $0.5 \text{ Mhz}$  (stability of the laser).

As previously mentioned the  $K = 2$  and  $3$  sub-bands are shifted by very weak resonances so they are analyzed separately.

For the other sub-bands all the Stark components were fitted with standard deviation better than  $0.3 \text{ mK}$ , allowing an increased accuracy for the value of the dipole moments of propyne.

INTRACAVITY SATURATION STARK SPECTROSCOPY OF OCS

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B E L G I Q U E

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F R A N C E

New Saturation Stark spectra of OCS have been recorded with the cell inside the cavity of a CO<sub>2</sub> laser. Close above threshold for sensitivity enhancement, the intracavity power is too low to observe the Lamb dip on the CO<sub>2</sub> fluorescence. So, the laser was stabilized on the maximum of the fluorescence Doppler profile with an absolute accuracy better than 300 kHz. Nevertheless, saturation was achieved on all the OCS transitions and the Lamb dips widths are always smaller than 1 MHz.

Thanks to voltages up to 100 kV/cm and sensitivity enhancement by a 100 factor, 41 new transitions have been added to the 47 ones previously measured with an extracavity set-up. The observation of transitions starting from higher excited vibrational states ( $\nu_1+\nu_2$  and  $3\nu_2$ ) and involving higher J values leads to an improved analysis of the Stark effect for OCS molecule, especially about vibrational and rotational dependence of the dipole moment.

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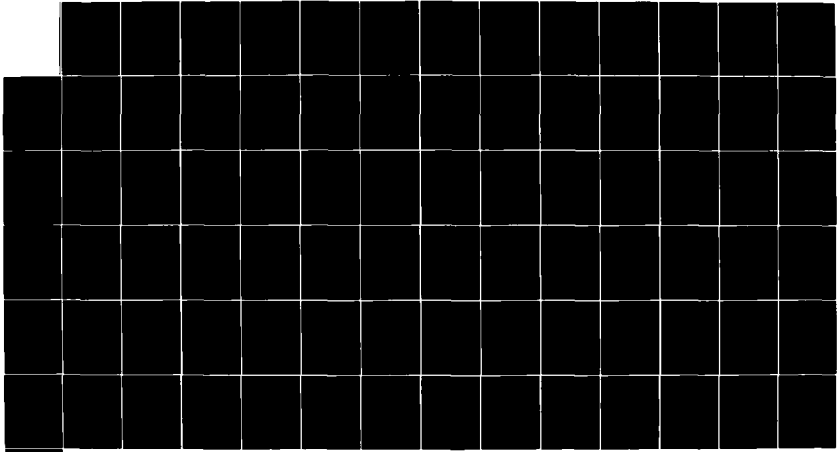
COLLOQUIUM ON HIGH RESOLUTION MOLECULAR SPECTROSCOPY  
(8TH) 19-23 SEPTEMBER (U) EUROPEAN OFFICE OF AEROSPACE  
RESEARCH AND DEVELOPMENT FPO NEW.. 23 SEP 83  
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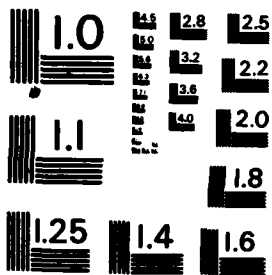
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Correlation diagrams for quasi-symmetric top  
molecules with a single rotor

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The rotation-bending-internal rotation hamiltonian for the  $MH_3NCY$  ( $M = C, Si, Ge$ ;  $Y = O, S, Se$ ) type molecules (A. Wierzbicki, J. Koput, and M. Kręglewski, *J. Mol. Spectrosc.* (1983), in press), which explicitly accounts for the kinetic coupling between rotation and two large amplitude motions, has been applied to calculate the correlations diagrams between the energy levels of molecules with a single rotor in the symmetric and asymmetric top limits. The potential function for bending vibration of the skeleton and for internal rotation has been taken as

$$V(\rho, \tau) = \frac{1}{2} k_{10} \rho^2 + K_B / c^2 + \rho^2 + \frac{1}{2} H \rho^3 \cos 3\tau$$

where  $\rho$  and  $\tau$  are bending and internal rotation coordinates, respectively. For fixed  $k_{10}$  and  $c^2$  values,  $K_B$  was changed in order to vary the height of the barrier to linearity from  $0 \text{ cm}^{-1}$  to  $6500 \text{ cm}^{-1}$ . The effect of hindered internal rotation (i.e.  $H \neq 0$ ) has been studied for various zero-barrier and low-barrier cases. The calculated expectation values of rotational constants show very strong dependence on the barrier height in the range from 0 to  $200 \text{ cm}^{-1}$ .

THE EMPIRICAL HARMONIC POTENTIAL FUNCTION  
OF DIBORANE

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A total of 114 spectroscopic data accumulated from six isotopic species of diborane have been used to permit a precise determination of the empirical potential function to be made for the first time. Thirty of the thirty three independent force constants can be determined with numerical significance. The physical significance of the values is probably best demonstrated by the rather close correspondence throughout with scaled *ab initio* force constants from two sources. All known frequency, B isotopic frequency shift, Coriolis  $\zeta$  and centrifugal distortion  $\Delta$  data are reproduced to high accuracy. Some applications made of the potential function are to achieve accurate analyses of a number of major Fermi resonance interactions present in the spectra, and to explain the anomalously small Coriolis interaction between the infrared active rocking and wagging fundamentals ( $\zeta^a < 0.1$ ) as compared with ethylene ( $\zeta^a \sim 0.45$ ). Calculated spectroscopic parameters are available.



EXACT ANALYTIC INITIAL VALUES FOR  
THE DIATOMIC ROTATIONAL HARMONICS

- Hafez KOBESSI

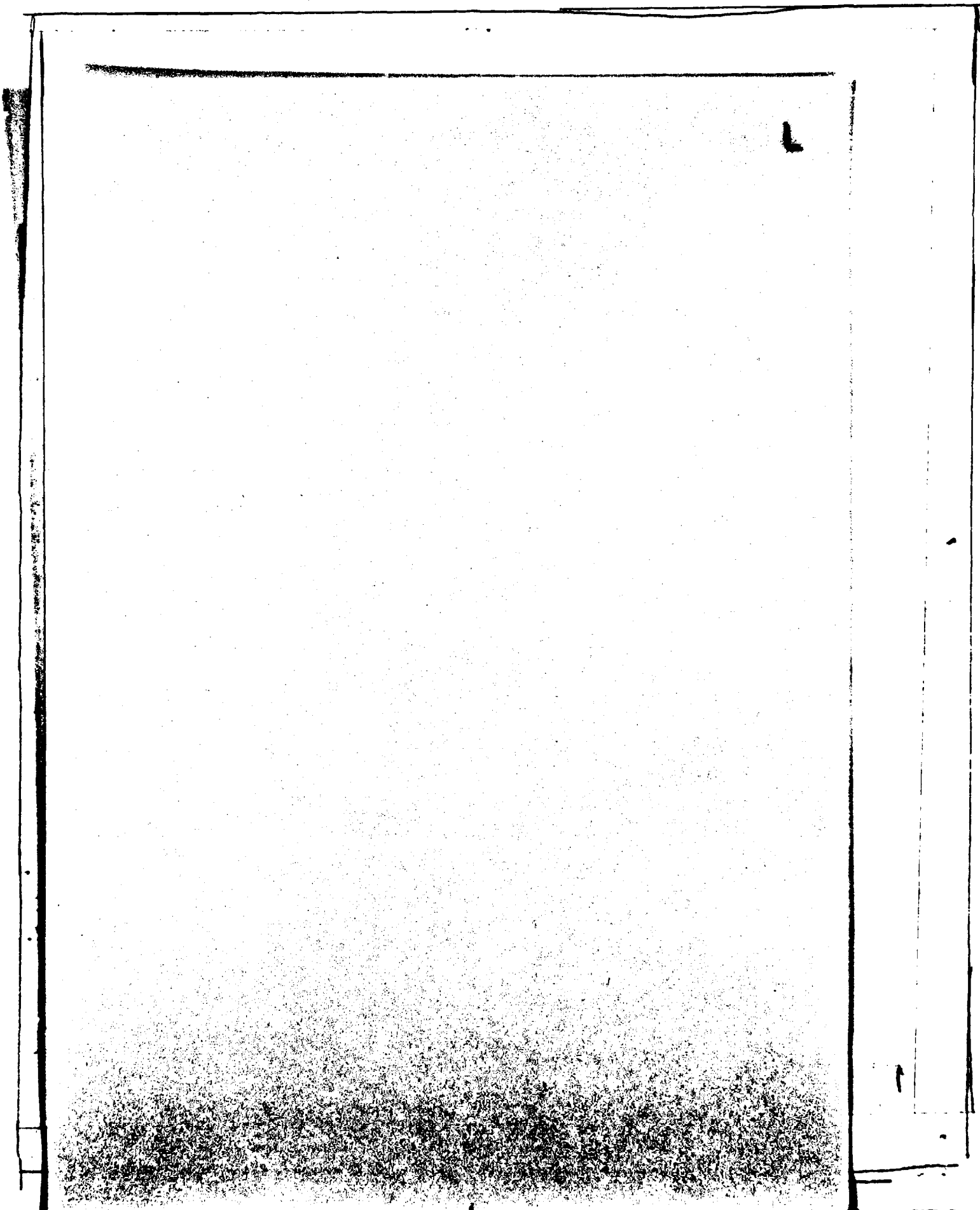
Faculty of Science, Lebanese University and the Group of Molecular  
and Atomic Physics at the National Research Council, Beirut, Lebanon

ABSTRACT:

A new contribution to the study of the rotation effect in the vibration-rotation diatomic wavefunction is presented. For a given vibrational level, the dependence of the wavefunction on the rotational quantum number  $J$  is given by:  $\psi_\lambda = \psi_0 + \lambda \phi_1 + \lambda^2 \phi_2 + \dots$  [with  $\lambda = J(J+1)$ ];  $\psi_0$  being the wavefunction of the pure vibration;  $\phi_1, \phi_2, \dots$  being the rotation harmonics (independent from  $J$ ) solutions of the rotational Schroedinger equations [H. Kobeissi, J. Physique 42 (1981) L 215]. It is proved that for any given potential, the initial values of  $\phi_1(r)$  at an

origin  $a$ , are:  $\phi_1(a) = 0$ ,  $\phi_1'(a) = \int_0^a \left( \frac{2\mu}{\hbar^2} B_v - \frac{1}{r^2} \right) \psi_0^2 dr$ , where  $B_v$

is the rotation constant. Similar results are derived for  $\phi_2(r), \phi_3(r) \dots$  where the initial values depend respectively on the distortion constants  $D_v, H_v, \dots$



AN ANALYSIS OF FIVE INTERACTING VIBRATIONAL STATES IN  $^{12}\text{CD}_4$ .

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In recent years the interacting rotational-vibrational states of the pentad ( $\nu_1$ ,  $\nu_3$ ,  $2\nu_2$ ,  $\nu_2 + \nu_4$ , and  $2\nu_4$ ) of  $^{12}\text{CH}_4$  have been studied through infrared and Raman spectra (1,2 and refs. therein). The two studies have used somewhat different Hamiltonian models and quite different calculational techniques in their approach to the problem, but both studies have led to fits of similar quality of the experimental data.

A study of the corresponding pentad states around  $2100\text{ cm}^{-1}$  in  $^{12}\text{CD}_4$  is now being undertaken, using as experimental data infrared spectra recorded by Guelachvili and Raman spectra recorded by Ouyoung and Esherick and by Brodersen. The computer program based on the theoretical model of Ref. 2 is used for the analysis, primarily because it runs very effectively on the computer used (a VAX 11/780).

This Hamiltonian model for the pentad contains 85 spectroscopic constants of which 22 are fixed to values determined from studies of the ground state and the  $\nu_2$  and  $\nu_4$  states (3). At present (May 1983) preliminary values of 38 constants can be determined by a least squares analysis of 1400 assigned lines through  $J' = 12$ . The overall standard deviation of the fit is  $0.011\text{ cm}^{-1}$ . Concurrently with the analysis an evaluation of the infrared line strengths is performed, leading to an estimation of the effective dipole moment parameters. In our poster we will present our recent results.

1. J.-E. Lolck, A.G. Robiette:  
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J.-E. Lolck, A.G. Robiette, L.R. Brown, R.H. Hunt:  
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J. Mol. Spectrosc., in press.
3. M. Loete, J.C. Hilico, A. Valentin, J. Chazelas, L. Henry:  
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DETERMINATION OF THE CUBIC FORCE FIELD OF NITROSYL FLUORIDE  
BY VIBRATION-ROTATION  $\alpha$  CONSTANTS AND SEXTIC CENTRIFUGAL  
DISTORTION CONSTANTS.

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The rotational spectra of nitrosyl fluoride (ONF) in the (100), (010) and (001) excited vibrational states were observed and the corresponding vibration-rotation  $\alpha$  constants determined. A centrifugal distortion analysis of 156 ground state rotational transitions yielded the values of all the sextic centrifugal distortion constants. Both vibration-rotation  $\alpha$  constants and sextic centrifugal distortion constants were used to determine, by least squares methods, the cubic part of the general valence force field of ONF. An ab initio calculation provided reliable constraints for the three cubic terms of the potential energy function which are not directly determinable by the available experimental data.

UN JEU UNIQUE DE 82 PARAMETRES POUR LE NIVEAU DE BASE, LA DYADE  $\nu_2$  ET  $\nu_5$  ET LA  
PENTADE  $\nu_1, \nu_4, 2\nu_2, \nu_2 + \nu_5$  ET  $2\nu_5$  DE  $^{12}\text{CH}_3\text{F}$ .

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La dyade et la pentade de  $^{12}\text{CH}_3\text{F}$  ont été réanalysées sur la  
base d'un Hamiltonien comportant tous les termes diagonaux et non diagonaux (à  
l'intérieur de chaque polyade) jusqu'à l'ordre 3 suivant la classification de  
AMAT-NIELSEN.

7 paramètres du niveau de base (dont 2 d'ordre 4) ont été fixés  
aux valeurs de la Réf (1), les 75 autres (16 relatifs à la dyade et 59 relatifs à  
la pentade) ont été ajustés simultanément par une méthode originale de moindres  
carrés pondérée à partir de trois sources de données expérimentales :

- 13 transitions microondes (2)
- 433 niveaux "observés" déduits des transitions IR de la  
Réf (3)
- 1 533 niveaux "observés" provenant des Réfs (4) et (5).

Ces diverses données ont été reproduites avec une précision  
de l'ordre de la précision expérimentale dans le domaine de "validité du modèle".  
Les avantages de la méthode (confirmés par les résultats obtenus) sont les sui-  
vants : 1) Cohérence : toutes les données expérimentales disponibles sont re-  
produites à partir d'un jeu unique de valeurs pour tous les paramètres.  
2) Fiabilité : les valeurs des paramètres prépondérants (d'ordre 0,1 et 2) sont  
peu dépendants de la valeur de J jusqu'à laquelle on pousse l'analyse.  
3) Précision : en général, l'écart type sur les paramètres est amélioré par rap-  
port aux études antérieures.

Plusieurs tests justifiant a posteriori la validité de la méthode proposée, seront  
présentés et discutés en même temps que le détail des résultats comparés à ceux  
d'études antérieures.

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USE AND PERFORMANCE IMPROVEMENT OF A COLOUR CENTER LASER FOR  
SPECTROSCOPY APPLICATIONS

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\* Gruppo Nazionale Struttura della Materia

The colour centre (CCL), lasers have attracted a considerable interest owing to their potential usefulness both in basic spectroscopy research and in applied research.

In our laboratory we have designed and built one CCL operating in the wavelength range 2.50-2.85  $\mu\text{m}$  and we use it for application to the spectroscopy of small molecules in the near infrared region.

It presently operates with a KCl:Li crystal ( $F_A(\text{II})$  colour centres) as the active medium and uses transverse injection of the  $\text{Kr}^+$  red line pump power [1].

A coated ZnSe beam-splitter placed at Brewster angle is now used to couple the pump radiation into the CCL resonator. Its reflectivity for the 647 nm line, perpendicularly polarized to the incidence plane, is about 98%. In this way we succeed in focussing about the whole pumping laser output-power on the crystal with very low losses for the i.r. radiation. To tune the laser wavelength we use a grating with 420 grooves/mm, blazed at 2.15 $\mu\text{m}$ , in a Littrow mount; the zeroth order reflection being the output beam. The fine tuning is accomplished by a tunable intracavity etalon with 79% reflectivity at 2.7 $\mu\text{m}$ . For a 15 GHz laser frequency scan we have so far obtained a resolution of about 500 MHz. Optoacoustic spectra of  $\text{CH}_3\text{OH}$ ,  $\text{HCOOH}$  and  $\text{CH}_3\text{COOH}$  molecules have been recorded. In all cases the observed transitions correspond to the OH-stretch fundamentals.

Furthermore we have measured, under constant experimental conditions, the fluorescence from the  $F_A(\text{II})$  centres of variously coloured crystals to improve laser performances.

[1] G. Baldacchini et al.

"Development of colour centre lasers for spectroscopy applications" *Revue Phys. Appl.* 18, 301, 1983

IR-MW double resonance measurements in two linear  
molecules

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Fed. Rep. Germany,

and

John Sheridan,

School of Molecular and Physical Sciences,  
UCNW, Bangor, U.K.

Direct  $\Lambda$ -type doubling transitions have been observed using infrared-microwave double resonance in  $\text{FC}^{15}\text{N}$  and DCCF. The measurements have allowed the determination of the constants  $q^0$  and  $q^1$  for both these molecules. The results for  $\text{FC}^{15}\text{N}$  are given below, those for DCCF will be given in the poster session.

In the case of DCCF the 12-16 9P(34)  $\text{CO}_2$  laser line has been found to be in coincidence with the R(0) transition of the  $\nu_3$  band (C-F stretch) of  $\text{D}^{13}\text{CCF}$ . This has allowed the determination of the rotational constant in the  $\nu_3=1$  state and the origin of the  $\nu_3$  band of this isotopic species.

<u><math>\text{FC}^{15}\text{N}</math></u>	<u>(0,1<sup>1</sup>,0)</u>	<u>(1,1<sup>1</sup>,0)</u>
$q^0$ (MHz)	18.4360	20.1713
$q^1$ ( $10^{-5}$ MHz)	4.98	0.06

RADIOFREQUENCY OPTOGALVANIC SPECTRUM OF H<sub>2</sub>

IN THE 700 n.m. - 780 n.m. REGION

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Electronic spectra of H<sub>2</sub> in the 700 n.m. - 780 n.m. region have been obtained by radiofrequency optogalvanic spectroscopy. The current resolution is about one wavenumber and is determined by the linewidth of the CR699 dye laser operating with LD700 dye in a standing wave configuration.

Almost all of the observed lines have been assigned to the (0,0), (1,1) and (2,2) bands of the D<sup>1</sup>Π<sub>u</sub> - E<sup>1</sup>Σ<sub>g</sub><sup>+</sup> transition and the (2,0) band of the B<sup>1</sup>Σ<sub>u</sub><sup>+</sup> - E<sup>1</sup>Σ<sub>g</sub><sup>+</sup> transition. Several other optically strong transitions are known to occur in the same spectral region but are not observed. The rotational 'temperatures' obtained from the rotational line intensities show a strong deviation from the equilibrium temperature of the gas and are found to be up to 150 K below room temperature.



THE DESLANDRES-D'AZAMBUJA SYSTEM OF  $^{13}\text{C}_2$  MOLECULE

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The spectrum of  $^{13}\text{C}_2$  has been photographed in emission from a hollow cathode discharge tube using a high resolution spectrograph. A detailed analysis of the bands, situated in the region 350–450 nm, has been carried out and the corresponding molecular constants for both upper ( $C^1\Pi_g$ ) and lower ( $A^1\Pi_u$ ) electronic states have been determined.

A comparison was made with the spectrum of  $^{12}\text{C}_2$  and the observed isotopic splitting is briefly discussed.

Laboratory and Astrophysical Determinations of the  
Radiative lifetime of  $\text{CH}^+$  ( $A^1\Pi$ ;  $v = 0$ )

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J. Sauval

Observatoire Royal de Belgique  
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B 1180 BRUXELLES, Belgique

The radiative lifetime of the  $A^1\Pi$  ( $v = 0$ ) state of  $\text{CH}^+$  has been measured on individual rotational lines of the (o-o) transition by a pulsed electron beam in  $\text{CH}_4$  and a single photon detection technique. A preliminary value has been obtained which is in better agreement with the solar photospheric determination than previous published values.

THE TRIPLET SYSTEM ( $A^3\Pi - X^3\Pi$ ) OF BN

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Institut d'Astrophysique - Université de Liège  
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The  $A^3\Pi - X^3\Pi$  transition of BN, first observed by Herzberg and Douglas in 1940 but only partially analyzed, has been observed under high resolution. A complete rotational analysis is given.

## THE SINGLET BANDS OF BN

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In 1940, three bands have been reported by Douglas and Herzberg as due to a singlet system of the BN radical but they have not been analysed. These bands have been recorded under high resolution and two of them have been rotationally analysed.

The first one at  $30963 \text{ cm}^{-1}$  is violet degraded and due to a  ${}^1\Sigma - {}^1\Pi$  transition. The second one at  $32817 \text{ cm}^{-1}$  is red degraded and due to a  ${}^1\Sigma - {}^1\Sigma$  transition. These two bands have the upper  ${}^1\Sigma$  state in common.

The third band at  $34498 \text{ cm}^{-1}$  is also red degraded but heavily overlapped by BCl bands. Nevertheless, it seems to be due to the 1-0 band of the  ${}^1\Sigma - {}^1\Sigma$  transition. This would lead to a  $\Delta G$  value of  $1681 \text{ cm}^{-1}$  for the excited state.

Molecular constants which have been determined are given below (in  $\text{cm}^{-1}$ ) :

- $\nu_0 (\Sigma - \Pi) = 30961.36$
- $\nu_0 (\Sigma - \Sigma) = 32792.34$
- B (upper  $\Sigma$  state) = 1.5578
- B (lower  $\Pi$  state) = 1.5446
- B (lower  $\Sigma$  state) = 1.6621

The Dipole Moment of Thioformaldehyde in its Singlet  
and Triplet  $\pi^*$ - $n$  Excited States.

by

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Laser induced fluorescence excitation has been used to measure Stark splittings of selected lines in the  $\tilde{A}^1A_2 + \tilde{X}^1A_1$  and  $\tilde{a}^3A_2 + \tilde{X}^1A_1$  band systems of  $H_2CS$  in electric fields up to 13 kV/cm. The derived excited state a-axis dipole moments are:  $0.820 \pm 0.007$  D for the  $4^1$  level of the  $\tilde{A}^1A_2$  state; and  $0.838 \pm 0.008$  D for the zeroth vibrational level of  $\tilde{A}^1A_2$ ; and  $0.534 \pm 0.015$  D for the zeroth vibrational level of the  $\tilde{a}^3A_2$  state. These results are compared with corresponding values of  $H_2CO$ , and interpreted in terms of the changing localisation of the  $\pi$  and  $\pi^*$  orbitals accompanying electronic excitation.

New Developments in Microwave  
Fouriertransform Spectroscopy

G.BESTMANN, H.DREIZLER, E.FLIEGE, W.KASTEN  
H.MÄDER and W.STAHL \*

We present the state of development of Microwave Fourier-  
transform Spectroscopy in the range of 5 to 18 GHz in our  
laboratory.

Extension of the frequency range is in progress. We will describe  
the possibility of Stark effect measurements and three and four  
level double resonance experiments.

These techniques will be illustrated by examples.

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High Resolution  
Microwave Spectrum of Propylfluoride.

W.KASTEN and H.DREIZLER\*

We reinvestigated the microwave spectrum of propylfluoride synclinal and antiperiplenar [1] with Microwave Fourier-transform spectroscopy [2,3] in the range of 8 to 18 GHz. We were able to resolve the internal rotation splittings of rotational transitions of the ground states of both forms. These splittings were analyzed by the internal axis method.

A determination of the barrier  $V_3$  to internal rotation, the moment of inertia  $I_{\alpha}$  of the methyl group and the angles between the inertia and internal rotation axes was possible.

A remeasurement with higher precision of the excited states is in progress.

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- [1] E.HIROTA, J.Chem. Phys. 37, 283 (1962).
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- [3] G.BESTMANN and H.DREIZLER, Z.Naturforsch. 37a, 58 (1982).

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Rotational Relaxation Studies by  
Microwave Spectroscopy.

H.MÄDER, H.BOMSDORF, and W.SCHREPP\*

New experimental techniques and theoretical developments concerning the study of rotational relaxation are presented.

The experimental methods partly involve the application of crossed microwave fields and pulse sequences for double resonance investigations by using conventional and bridge type spectrometers.

Examples are given and discussed.

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Pressure and Linewidth Measurements of the Pure Rotation Raman Spectra of Nitrogen and Oxygen

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Abstract

The study of pressure-broadened rotational Raman spectra is valuable for probing molecular environments and for the examination of gas-phase collision processes. We report measurements of the self- and foreign-gas broadening of the Stokes pure rotation Raman lines of nitrogen and oxygen for the pressure range of 1-60 bar using helium as the foreign gas.

Spectra were recorded using an argon-ion laser with a nominal power of 5W at 488.0 nm and a three-metre Czerny-Turner scanning monochromator with a reciprocal linear dispersion of  $1.4 \text{ cm}^{-1}\text{mm}^{-1}$ . The scanning of the monochromator and the acquisition of spectral data were controlled by a Nicolet 1180 system.

A typical example of the effect of increasing pressure on the rotational lines is shown in Figure 1 for the S(4) line of nitrogen at 300 K over the pressure range 10-60 bar. Plots of FWHM against pressure for the nitrogen lines are illustrated in Figure 2.

Comparisons of our experimental results are made with previously reported experimental values and with theoretical predictions.

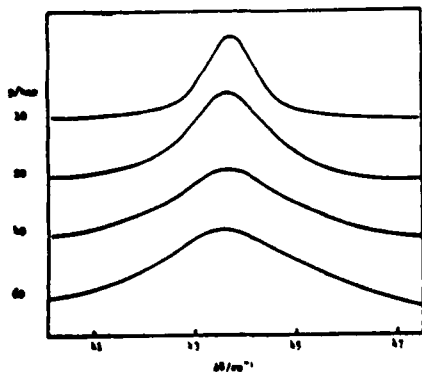


Figure 1. Raman spectra of S(4) of  $\text{N}_2$  at 300 K and 10 - 60 bar pressure.

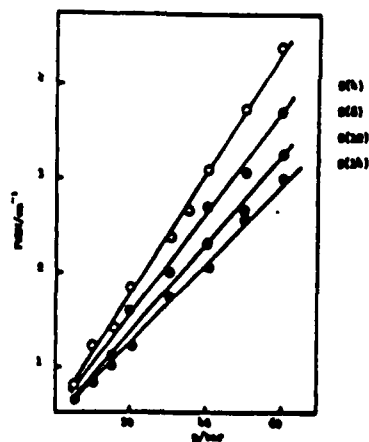


Figure 2. Plot of FWHM against pressure for  $\text{N}_2$  at 300 K.

Spectres microonde de SF<sub>5</sub>Cl dans les états excités

$$v_6(B_1) = 1 \text{ et } v_{11}(E) = 1$$

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Les spectres de SF<sub>5</sub>Cl (groupe C<sub>4v</sub>) ont été mesurés à 35 GHz, 70 GHz, 200 GHz, correspondant aux transitions J = 8 → 9, J = 9 → 10, J = 17 → 18, J = 18 → 19, J = 19 → 20, J = 55 → 56 et J = 57 → 58. Contrairement à ce qui a été observé pour BrF<sub>5</sub> et IF<sub>5</sub> ces spectres ne présentent pas de résonance de Coriolis. Les transitions relatives à v<sub>6</sub> = 1 ont été identifiées et les paramètres correspondant déterminés. Du fait de la complexité des spectres relatifs à v<sub>11</sub> = 1 seules quelques transitions identifiées sont utilisées pour obtenir une première estimation des paramètres.

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ANALYSIS OF THE HIGH-RESOLUTION CARS SPECTRUM OF THE Q-BRANCH OF THE  
 $\nu_1$  BAND OF AMMONIA

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The Q-branch of the  $\nu_1$  Raman band of ammonia  $^{14}\text{NH}_3$  at a pressure of 15 mbar has been recorded with the high-resolution cw CARS spectrometer in Munich (1,2) at an instrumental resolution of  $0.001 \text{ cm}^{-1}$ , resulting in an observed linewidth of about  $0.015 \text{ cm}^{-1}$  due to Doppler- and residual pressure broadening. The wavenumber accuracy was estimated to be  $0.01 \text{ cm}^{-1}$  on an absolute scale.

Practically all the observed lines could be assigned to transitions between energy levels that were determined recently through an analysis of so far unpublished infrared Fourier transform ( $0.01 \text{ cm}^{-1}$  resolution) and grating spectra ( $0.03 \text{ cm}^{-1}$  resolution) of the  $\nu_1$  band (3). The deviations between predicted and observed wavenumbers are smaller than  $0.02 \text{ cm}^{-1}$  with few exceptions, and without taking into account the corrections due to the asymmetry of CARS line profiles.

Considering the symmetry properties of the  $\text{NH}_3$  molecule within the framework of the permutation-inversion group, the line-strengths in the Raman spectrum are calculated. The resulting computer simulated CARS spectrum will be compared with the observed spectrum.

- (1) H. Frunder, D. Illig, T. Rabenau, W. Bachmann, and H.W. Schrötter, in: Raman Spectroscopy Linear and Nonlinear (J. Lascombe and P.V. Huong, Eds.), Wiley-Heyden, Chichester 1982, p. 193
- (2) H. Frunder, D. Illig, A. Beckmann, and H.W. Schrötter, Poster at this conference
- (3) B. Brault, K. Narahari Rao, Š. Urban, D. Papoušek, in preparation

DIODE LASER SPECTRA OF ETHYLENE IN THE 11.8  $\mu\text{m}$  REGION

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B E L G I Q U E

Diode laser spectra of ethylene have been recorded between 883 and 833  $\text{cm}^{-1}$  using the Diode Laser Spectrometer of the Laboratoire de Spectroscopie Moléculaire of the Facultés Universitaires N.D. de la Paix à Namur. A set of 2000 lines have been measured with an absolute precision between 0.0005 and 0.002  $\text{cm}^{-1}$ . A pathlength of 52 m allows the observation of very weak absorption lines.

The main interest of this study was to assign the low  $K_a$  series of the very weak  $\nu_{10}$  vibrational band. The main intensity of  $\nu_{10}$  indeed comes from  $\nu_7$  through an a-type Coriolis coupling increasing with  $K_a$  so that the low  $K_a$  series are too weak to be observed in F.T. spectra. On the basis of these new assignments an improved analysis of the 10  $\mu\text{m}$  interacting bands system ( $\nu_7$ ,  $\nu_{10}$  and  $\nu_4$ ) has been performed and the results will be discussed.

Furthermore, the determination of the low  $K_a$  series of  $\nu_{10}$  is of prime interest because  $\nu_{10}$  is the lower state of the first hot band reaching the  $\nu_7 + \nu_{10}$  level. (This result will be discussed in another communication at the Congress).

From the observation of the  $K_a=0$  and 1 series of  $\nu_{10}$ , the own intensity of this band has been determined to be  $17.500 \pm 2.500$  times smaller than the  $\nu_7$  one.

The  $\nu_2$ ,  $2\nu_2 - \nu_2$  and  $\nu_4$  Bands of  $\text{ND}_3$

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The ir absorption spectrum of gaseous  $\text{ND}_3$  between 500 and 1300  $\text{cm}^{-1}$  has been recorded on the Bomem DA 03.002 present at the N.R.C., Ottawa, with a resolution of about 0.005  $\text{cm}^{-1}$ . Transitions belonging to the  $\nu_2$  and  $\nu_4$  bands have been measured and assigned, while for the  $2\nu_2 - \nu_2$  band only the Q branches have been identified. The effective spectroscopic parameters and the interaction constants between  $\nu_2 = 1$  and  $\nu_4 = 1$  vibrational states have been obtained.

At the same time the inversion rotation spectrum of  $\text{ND}_3$  has been recorded in the far ir on two different FT Spectrometers:

- i) the FT instrument present at IROE, Firenze, with a resolution of about 0.005  $\text{cm}^{-1}$  in the region 8-80  $\text{cm}^{-1}$ ;
- ii) the Bomem spectrometer with a resolution of about 0.006  $\text{cm}^{-1}$  in the region 60-200  $\text{cm}^{-1}$ .

These measurements together with the combination differences derived from the  $\nu_2$  and  $\nu_4$  fundamentals and the pure inversion (1,2) and inversion-rotation measurements (3) should give very precise values for the ground state constants.

- 1) R.G. NUCKOLLS, L.J. RUEGER AND H. LYONS. Phys.Rev. 89, 1101, 1953.
- 2) G. HERRMANN. J.Chem.Phys. 29, 875, 1958.
- 3) G.E. ERLANDSSON AND W. GORDY. Phys.Rev. 106, 513, 1957.

FLUOROFORM : ANALYSIS OF THE 8-9 MICRONS POLYAD

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We have recorded the Fourier Transform infrared spectrum of  $\text{CF}_3\text{H}$  between 1000 and 2000  $\text{cm}^{-1}$  with a resolution of 0.005  $\text{cm}^{-1}$ . In the region 1110-1250  $\text{cm}^{-1}$  it has been shown earlier (1) (2) that 3 interacting bands are involved, namely  $\nu_2$  (1141  $\text{cm}^{-1}$ ),  $\nu_5$  (1158) and  $\nu_3+\nu_6$  (1208  $\text{cm}^{-1}$ ). The two former are linked through a strong X-Y type Coriolis resonance. The last one is somewhat similar to  $\nu_6$  (3) by the fact that a very small value of  $B_6-C_6+(C\zeta)_6$  entails a considerable effect of the  $l(2,2)$  resonance throughout the band. Moreover  $\nu_5$  and  $\nu_3+\nu_6$  are linked by a Fermi interaction. Therefore it seemed possible to treat the problem by diagonalizing 5 x 5 blocks corresponding to a given value of  $k-l$ .

The assignment of transitions in this spectrum was extremely difficult due to these interactions and to the density of lines (about 6000 peaks for 20 000 predicted transitions). Guided by computer programmes including all the resonances, we could assign successively transitions of  $\nu_3+\nu_6$ , then  $P_{R_K}$  and  $R_{R_K}$  lines of  $\nu_5$  up to  $K = 24$ . The fitting of these data pointed out the need for another interaction term between the neighbouring  $(k-l)$  blocks. This was successfully approximated by a  $(\Delta l = 2, \Delta k = -1)$  perturbation involving only the  $(k, l = -1)$  and  $(k+1, l = -1)$  states of  $\nu_5$ . Thereafter, it was possible to assign  $\nu_5$  above its crossing point with  $\nu_2$  and also to assign the transitions in  $\nu_2$ . Molecular constants will be given for all these levels.

- (1) P. LOCKETT and P.M. WILT, J. Chem. Phys. 60, 3203 (1974).
- (2) N. FYKE, P. LOCKETT, J.K. THOMPSON and P.M. WILT, J. Mol. Spectrosc. 58, 87 (1975).
- (3) G. GRANER, R. ANTILLA and J. KAUPPINEN, Mol. Phys. 38, 103 (1979).

Analyse de la transition  $\nu_3 - \nu_1$  du disulfure de carbone à partir de spectres obtenus à l'aide d'un spectromètre à grilles et d'un spectromètre à diode-laser.

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Les enregistrements de la transition  $00^0_1-10^0_0$  du  $^{12}\text{C}^{32}\text{S}_2$  et  $^{12}\text{C}^{34}\text{S}_2$  (échantillon enrichi à 90 % en  $^{34}\text{S}$ ) ont été obtenus à l'aide d'un spectromètre à grilles de type Girard (résolution de  $0,07\text{ cm}^{-1}$ , précision de  $0,002\text{ cm}^{-1}$  sur les pics isolés).

Les résultats des analyses sont :

	$\nu_0 (\text{cm}^{-1})$	$\Delta B (10^{-5} \text{cm}^{-1})$	$\Delta D (10^{-8} \text{cm}^{-1})$
$^{12}\text{C}^{32}\text{S}_2$	877,3564 $\pm 0,004$	- 60,8507 $\pm 0,05$	- 0,04 $\pm 0,004$
$^{12}\text{C}^{34}\text{S}_2$	889,2347 $\pm 0,003$	- 51,9914 $\pm 0,03$	- 0,007 $\pm 0,002$

Cette étude préliminaire a été poursuivie à l'aide d'un spectromètre à diode-laser. Cet appareil est équipé d'une cellule à réflexions multiples ce qui permet d'éviter tout élargissement dû à la pression. Les conditions expérimentales étaient les suivantes : parcours 52 m, pression  $5 \cdot 10^{-1}$  mbar. Le spectromètre est couplé à un miniordinateur HP1000 qui pilote le balayage en fréquence, acquiert les données et en assure le traitement. La calibration a été réalisée à partir des raies bien connues de la bande  $\nu_1$  d'OCS [1], la précision absolue obtenue est meilleure que  $0,001\text{ cm}^{-1}$ .

A l'heure actuelle, 30 % des raies observées ont été identifiées. Les transitions suivantes ont été observées :  $00^0_1-10^0_0$ ,  $01^1_1-11^1_0$ ,  $02^1_1-12^1_0$ ,  $10^1_1-20^1_0$ .

[1] J.S. WELLS, F.R. PETERSEN, A.G. MAKI, and D.J. SUKLE, Appl. Opt., 20, 1676-1684 (1981).

ANALYSE DES BANDES  $\nu_2 + \nu_3^{\pm 1}$  ET  $\nu_1 + \nu_2$  DE  $^{14}\text{NH}_3$

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Le spectre de  $^{14}\text{NH}_3$  a été enregistré à l'aide d'un spectromètre à transformée de Fourier dans l'intervalle spectral 3 900 - 4 600  $\text{cm}^{-1}$  avec une résolution de 0,007  $\text{cm}^{-1}$ .

Nous avons analysé la structure des bandes  $\nu_2 + \nu_3^{\pm 1}$  et  $\nu_1 + \nu_2$ , les autres bandes apparaissant dans cette région étant trop peu intenses pour être étudiées correctement.

*Bande  $\nu_2 + \nu_3^{\pm 1}$*

Les raies de cette bande ont été identifiées jusqu'à  $J = 10$  dans la composante  $s \rightarrow s$  et jusqu'à  $J = 12$  dans la composante  $a \rightarrow a$ . Dans l'expression des énergies des niveaux supérieurs développées jusqu'au sixième ordre d'approximation, nous n'avons tenu compte que des résonances essentielles ( $k - l = 3$ , dédoublement du type 1) et de la résonance de Coriolis avec la bande  $\nu_1 + \nu_2$ . Nous avons pu ainsi obtenir, pour chacune des composantes, un ensemble de constantes spectroscopiques qui permet de retrouver la position des raies avec une bonne précision.

*Bande  $\nu_1 + \nu_2$*

Les raies de cette bande ont été observées jusqu'à  $J = 10$ . Pour déterminer les constantes spectroscopiques, nous avons utilisé l'expression classique des fréquences d'une bande parallèle développée jusqu'au quatrième ordre d'approximation.



Rovibrational Analysis of the  $\nu_7$  in Diazirine:  $\text{H}_2\text{C} \begin{array}{l} \diagup \text{N} \\ \diagdown \text{N} \end{array}$

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Within the framework of research concerning the determination of the molecular constants of diazomethane and its structural isomers by means of microwave, millimeter wave and infrared Fourier-transform spectroscopy, I shall report the rovibrational analysis of the  $\nu_7$  fundamental vibrational mode of diazirine. The infrared spectra of diazirine and of the substituted isotopic species  $\text{D}_2\text{CN}_2$ ,  $\text{H}_2^{13}\text{CN}_2$  and  $\text{H}_2\text{C}^{15}\text{N}_2$  have been recorded and a complete analysis of the  $\nu_3$  fundamental of the main species was carried out (1).

The  $\nu_7$  fundamental at  $807.13 \text{ cm}^{-1}$  ( C-N asymmetric stretching ) is a B-type band and presents a complicated pattern since diazirine is an asymmetric rotor with  $\kappa = -0.427$ . The characteristics of such a band are the combinations of A-type and C-type transitions. The central part of the spectrum contains the strongest transitions  $J_{0,J} \leftrightarrow (J+1)_{1,J+1}$  and  $J_{1,J} \leftrightarrow (J+1)_{0,J+1}$  while in the extreme wings of the P- and R-branches the strongest lines are due to the transitions  $J_{J,0} \leftrightarrow (J+1)_{J+1,1}$  and  $J_{J,1} \leftrightarrow (J+1)_{J+1,0}$ . Using the molecular constants for the ground state obtained from microwave and millimeter wave spectra (2), the rovibrational assignment and the determination of the molecular constants for the state  $\nu_7=1$  were possible and will be reported here.

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1) A. Gambi, M. Winnewisser and J.J. Christiansen,  
J. Mol. Spectrosc. 98, (1983), in press.

2) M. Bogey, M. Winnewisser and J.J. Christiansen,  
To be published.



PREDICTION FOR MAGNETIC DIPOLE TRANSITIONS IN THE GROUND STATE OF SF<sub>6</sub>

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ABSTRACT

We have theoretically investigated the possibilities of observing magnetic dipole transitions in the ground vibrational state where electric dipole transitions are strictly forbidden for O<sub>h</sub> molecules<sup>(1)</sup>.

The magnetic dipole moment operator is the sum of two operators, m<sub>s</sub> associated with nuclear spins and m<sub>R</sub> associated with the rotational motion of the molecule. In the rigid model however none of these operators gives rise to transitions with  $\Delta J \neq 0$ . We have thus looked first for transitions with  $\Delta J = 0$  and second for transitions with  $\Delta J \neq 0$  which could be induced by higher order effects.

1) Transitions with  $\Delta J = 0$

In that case we have taken into account the clustering of the rotational levels and the strong mixing of states belonging to the same cluster<sup>(2)</sup>; the moments of transitions between the hyperfine sublevels within a cluster have then an order of magnitude comparable to the diagonal matrix elements of the dipole operator. For these transitions m<sub>s</sub> is the more important operator; the frequencies range up to about 500 kHz.

2) Transitions with  $\Delta J \neq 0$

We have analysed two possibilities for these transitions to arise; first the mixing of states with different J due to hyperfine interactions, second the deformation of the molecule. This deformation was taken into account by applying a contact transformation to the rotational moment m<sub>R</sub> expanded along the normal coordinates; the transformed moment has indeed non-zero matrix elements with  $\Delta J = \pm 1$  but these transitions are extremely weak. The effects of hyperfine mixing were estimated through a first order perturbation calculation only but they do not lead to much stronger transitions.

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1983 INTERNATIONAL COLLOQUIUM ON HIGH RESOLUTION  
MOLECULAR SPECTROSCOPY

Application of Direct Numerical Diagonalization  
Techniques to Linear Triatomic Molecules

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The Direct Numerical Diagonalization (DND) technique has been utilized for the study of the band strengths of a linear triatomic molecule: CO<sub>2</sub>. Sets of basis states have been chosen to include asymptotic dissociation behavior as well as a reasonable fit to equilibrium data appropriate to each independent normal mode. The DND method has been used for the determination of the initial basis sets as well as for the final multi-dimensional problem. The potential for CO<sub>2</sub> has been determined by a least-squares fitting procedure of the DND eigenvalues to experimental energies. The eigenvectors resulting from the diagonalization are used to similarity transform the dipole moment matrix formed from a Taylor series expansion of the dipole moment operator. Inaccuracies due to lack of basis set completeness (finiteness of the Hamiltonian and dipole moment matrices) and due to truncation of the potential and dipole moment expansions are discussed. The solution of the Hamiltonian (mechanical problem) is thus utilized to transform dipole derivatives into transition moments. Inversion of this transform allows the calculation of dipole moment coefficients. "Hot" and difference band strengths can then be determined from ground state overtone and combination band strength data. Methods of dealing with the sign ambiguities arising from determining the transition moments as square roots of band strengths are discussed. Comparison of the final eigenstate energies with those determined by the twice-contact transformed Hamiltonian method is shown. Results for the eigenvectors and calculated band strengths (especially the combination vs difference band strengths) are compared with Suzuki's DND work.<sup>1</sup> Extension of this technique to the calculation of individual line intensities is covered as well.

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NONADIABATIC CONTRIBUTIONS TO THE DIPOLE MOMENTS OF  ${}^7\text{LiH}$  AND  
 ${}^7\text{LiD}$  IN THE A  ${}^1\Sigma^+$  STATE

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Recent determinations of electric dipole moments in the A  ${}^1\Sigma^+$  state of  ${}^7\text{LiH}$  and  ${}^7\text{LiD}$  have revealed a disagreement in the theoretical predictions for the electric dipole moments of both species. The origin and magnitude of this disagreement will be discussed in context with nonadiabatic coupling between the A and the X state.

Multiphoton Ionisation Spectroscopy of H<sub>2</sub>O and H<sub>2</sub>S

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The Rydberg states of small polyatomic molecules generally lie at excitation energies corresponding to vacuum ultraviolet (VUV) wavelengths. Multiphoton ionisation (MPI) spectroscopy provides a complementary method for studying these highly excited electronic states, being particularly sensitive towards longer lived, predissociating states. Examples drawn from our ongoing studies involving the molecules H<sub>2</sub>O, H<sub>2</sub>S and their respective deuterated analogues will be presented. These highlight the potential of MPI for revealing structured spectra associated with excited electronic states, hitherto unobserved because either

- (i) they arise via transitions forbidden by one photon, electric dipole selection rules (e.g. the <sup>1</sup>A<sub>2</sub> excited states of H<sub>2</sub>S and D<sub>2</sub>S) or,
- (ii) they possess relatively low oscillator strength and, as such, lie buried beneath regions of more intense, apparently continuous absorption in the conventional one photon VUV absorption spectrum. The repulsive excited states giving rise to these continua (which often dominate molecular absorption spectra), being so short lived, do not show up in MPI spectra.

Laser Magnetic Resonance Rotational Spectroscopy of  $^2\Sigma$  Radicals:  
Ethyne (CCH)

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The measurement of the  $N = 6-7$  rotational transition of the ground  $^2\Sigma^+$  state of CCH by the method of laser magnetic resonance is reported. A theoretical formalism for the prediction and analysis of gas-phase magnetic resonance spectra of  $^2\Sigma$  electronic states is presented. Transition frequencies, linewidths, and intensities of the transitions are computed as a function of magnetic flux density, and the absorption coefficient at each field point is then computed to synthesize the magnetic resonance spectrum. The theoretical formalism combined with molecular parameters from microwave and astronomical data is used to analyze the laser magnetic resonance spectrum of CCH. A combined least squares analysis of existing microwave, astronomical, and the present LMR spectroscopic data is carried out to determine the optimum set of molecular parameters.

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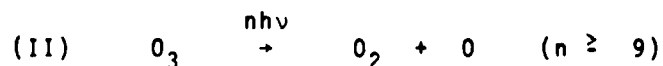
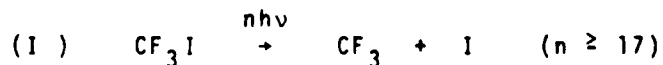
Dynamics of IR-Multiphoton Excitation of Polyatomic Molecules  
from High Resolution Spectroscopy

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The dynamics of IR-Multiphoton excitation of polyatomic molecules is investigated experimentally and theoretically with particular emphasis on nonlinear effects and their frequency dependence. Two model reactions have been studied:



Experiments demonstrate conclusively a nonlinear intensity effect in the case of off-resonant excitation of  $\text{CF}_3\text{I}$ . A similar frequency dependence of the nonlinearity is theoretically predicted for  $\text{O}_3$  by quantum mechanical calculations for the excitation process in the quasiresonant approximation using most recent data from the high resolution spectra of  $\text{O}_3$ . We present also the first approximate quantum calculations for the IR-photochemical reaction (II).

The results are discussed in terms of their dependence upon spectroscopic parameters and rotational effects as well as in relation to statistical mechanical concepts for IR-photochemistry and to experiments postulating a collision free reaction (I).



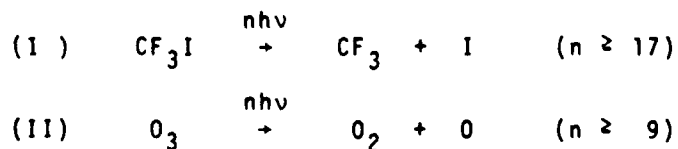
Dynamique de l'excitation multiphotonique de molécules polyatomiques dans l'infrarouge à partir de la spectroscopie à haute résolution

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La dynamique de l'excitation multiphotonique infrarouge de molécules polyatomiques est expérimentalement et théoriquement explorée en portant particulièrement l'accent sur les effets non linéaires et leur dépendance de la fréquence. Deux réactions modèles ont été étudiées:



Dans le cas d'une excitation hors résonance du  $\text{CF}_3\text{I}$ , un effet d'intensité non linéaire est expérimentalement démontré. De très récentes données fournies par la spectroscopie à haute résolution de l'ozone sont exploitées par des calculs quantiques pour le processus d'excitation dans l'approximation quasirésonnante; une dépendance similaire de la fréquence pour la nonlinéarité est ainsi théoriquement prédite pour  $\text{O}_3$ . De surcroît, les premiers calculs quantiques approchés pour la réaction photochimique (II) seront présentés.

L'influence des paramètres spectroscopiques et des effets rotationnels est incluse dans la discussion des résultats. Nous établirons leurs relations avec, d'une part, des concepts de mécanique statistique pour la photochimie IR et, d'autre part, des expériences postulant un mécanisme réactionnel libre de toutes collisions.

LASER PREDISSOCIATION SPECTRUM OF  $\text{PH}^+(\text{A}^2\Delta + \text{X}^2\Pi)$ .  
RESOLUTION OF PROTON AND  $^{31}\text{P}$  HYPERFINE STRUCTURE

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The (0-1) and (1-2) bands of the  $\text{A}^2\Delta + \text{X}^2\Pi$  system of  $\text{PH}^+$  have been recorded in a laser/ion beam experiment at a resolution of  $1 \text{ cm}^{-1}$ . The spectrum was obtained by the detection of the fragment  $\text{P}^+$  ions which arise from weak predissociation of the  $^2\Delta$  state. Rotational levels with  $N' < 13$  of  $v' = 0$  lie below the dissociation limit, and this leads to a sharp 'breaking on' in the rotational branches of the 0-1 band at  $N' = 13$ . Our data has been merged with the optical emission data on the (0,0), (0-1), ( $N' < 13$ ) and (1-0) bands [1], together with a remeasurement of the (0-1) band [2], to provide an improved set of molecular constants for  $v' = 0$  and 1, and  $v'' = 0, 1$  and 2 of the  $\text{A}^2\Delta$  and  $\text{X}^2\Pi$  states respectively.

The Doppler width in the fast beam is sufficiently low to permit resolution of  $^{31}\text{P}$  and  $^1\text{H}$  hyperfine structure. We have recorded over fifty rotational lines in the 1-2 band using a single mode dye laser, and have obtained complete sets of hyperfine parameters for both nuclei in both the  $\text{X}^2\Pi$  and  $\text{A}^2\Delta$  states.

1. N.A. Narasimham, Can. J. Phys., 35, 901 (1957).
2. 0-1 band re-photographed at NRC, Ottawa, July 1982.

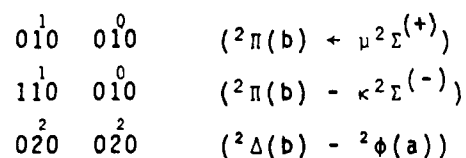
HIGH RESOLUTION ANALYSIS OF THE BENDING VIBRATIONAL  
MODE TRANSITIONS IN THE  $\tilde{A}-\tilde{X}$  SPECTRUM OF  $N_2O^+$

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Fast ion beam laser spectroscopy (FIBLAS) is applied to the study of the transitions involving the bending vibrational mode of the near ultraviolet  $\tilde{A}-\tilde{X}$  system of  $N_2O^+$ .

Detection of the molecular photofragment resulting from a slow predissociation of the excited state leads to high spectral resolution of the molecular fine and hyperfine structure(1). The following transitions have been observed



As a result, we shall present :

- 1) a study of the vibronic interactions (Renner-Teller effect) of the ground  ${}^2\Pi$  state of  $N_2O^+$
- 2) an interpretation of the hyperfine structure of the first excited state  $\tilde{A}{}^2\Sigma^+$
- 3) the determination of a set of molecular constants.

Reference :

- (1) S.ABED, M.BROYER, M.CARRÉ, M.L.GAILLARD and M.LARZILLIERE,  
Chem.Phys. 74, 97 (1983)



FOURIER SPECTROSCOPY OF THE  $^{13}\text{C}_2$  AND  $^{12}\text{C}^{13}\text{C}$  Phillips, Ballik-Ramsay  
AND Swan ELECTRONIC SYSTEMS

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First laboratory observation of the  $^{13}\text{C}_2$  and  $^{12}\text{C}^{13}\text{C}$  is presented. The radicals have been produced in a microwave discharge through  $^{13}\text{CO}$  or  $^{12}\text{CO} + ^{13}\text{CO}$  gas. The spectra were recorded between  $3000\text{ cm}^{-1}$  and  $22\,000\text{ cm}^{-1}$  with a high resolution Fourier Transform interferometer. The stonger emission bands have been analyzed : (0-0) and (1-0) bands of the Phillips system (1), (0-0) bands of the Ballik-Ramsay (2) and Swan (3) systems. Accurate molecular parameters have been derived using the direct approach method . Rotational perturbations are observed for both isotopic species in the  $b^3\Sigma(v=0)$ ,  $A^1\Pi(v=1)$  and  $d^3\Pi(v=0)$  levels.

- (1) C. AMIOT, J. VERGES  
Astr. and Astr. Suppl. Series 51, 257 (1983).
- (2) C. AMIOT, J. VERGES  
The Astr. J. 263, 993 (1982).
- (3) C. AMIOT  
The Astr. J. 52, ... (1983).

INVESTIGATIONS OF PERTURBED STATES OF BaO BY UV-LASERSPECTROSCOPY

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The potential energy curves of BaO for electronic states in the region above  $32000\text{ cm}^{-1}$  are not well known. Only the minimum of the C  $^1\Sigma^+$  - and D  $^1\Sigma^+$ -state has been measured with the Optical-Optical-Double-Resonance spectroscopy /1/. Our highly resolved UV-laser experiments show a lot of perturbed vibrational bands. The analysis of these bands leads to numerous well defined heterogeneous and homogeneous perturbations. Our systematic recordings of the rotational finestructure show additional perturbations compared to the observations by OODR /1/. Evaluations of the perturbation parameters provide informations about spectroscopic constants of still unknown electronic states.

/1/ R. A. Gottscho, P. S. Weiss and R. W. Field;  
J. Mol. Spectrosc. 82, 283 (1980)

Emission spectrum assigned to HCCS

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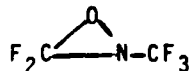
2 National Research Council, OTTAWA.

The emission spectrum observed by a R.F. discharge through Thiophen is compared to the absorption spectrum previously obtained by the flash photolysis technique and thought to be due to the HCCS free radical (1).

The structure with P and R branches which is consistent with a linear molecule does not allow unique rotational assignments. Some results are given in the best cases. Assumptions are done on the vibrational frequencies in agreement with the previous identification.

(1) KRISHNAMACHARI S.L.N.G. and RAMSAY D.A.  
Far. Disc. Chem. Soc. 71, 205-12 (1981).

MICROWAVE SPECTRA AND NORMAL COORDINATE ANALYSIS OF



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Microwave spectra of the vibrational ground state and four excited states of the lowest normal vibration have been studied between 10 and 49 GHz.

Watsons quartic Hamiltonian operator was used to fit the rotational and centrifugal distortion constants to the measured transitions up to  $J = 49$ .

Dipole moment components were calculated from lines, split by the second order Stark effect. The frequency of the internal rotation normal vibration was estimated from the line intensities of the different vibrational species.

Infrared and far infrared spectra were recorded and the measured frequencies assigned.

A normal coordinate analysis will be presented.



MILLIMETER WAVE SPECTRUM OF  $^{17}\text{O}_2$ . MAGNETIC HYPERFINE  
STRUCTURE AND QUADRUPOLE COUPLING CONSTANTS.

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The report deals with the result of the observation and the analysis of the  $^{17}\text{O}_2$  spectrum in the region 56-120 GHz.

The sequence of the rotational levels of a  $^3\Sigma$  state depends upon the values of the rotational constant B and of the spin-spin coupling constant  $\alpha$ . In the case of oxygen the separation of the energy levels within a triplet in which each rotational level with a given values of the rotational quantum number N is split, is very similar so that all the transitions with  $\Delta N=0$  and  $\Delta J=\pm 1$ , except the  $J=1-0$ , fall in the 5 mm region giving rise to the well known fine structure spectrum of oxygen.

The spectrum is much more complicate when both nuclei have spin 5/2. In this case six stacks of levels are possible since the vectorial addition of the  $I=5/2$  spins of both  $^{17}\text{O}$  nuclei gives a total nuclear spin  $I_T=5,4,3,2,1,0$ .

Because of the symmetry of the  $^{17}\text{O}_2$  nuclear spin functions the rotational levels of even N can only be associated with odd values of  $I_T$  and odd values of N with even values of  $I_T$ . Taking into account the transitions related to the selection rules  $\Delta N=0$ ,  $\Delta I=0$ ,  $\Delta J=\pm 1$ ,  $\Delta F=0, \pm 1$  a number of about 800 lines can be predicted to lie in the region 56-64 GHz with the right strength to be detected with our spectrometer.

In fact about 600 lines have been observed and assigned while the remaining have been disregarded because overlapped by other  $^{17}\text{O}_2$  transitions or by transitions due to the different isotopic species of oxygen present in the sample. The analysis of the experimental line frequencies by means of a computer program expressly written yields the molecular parameters of  $^{17}\text{O}_2$  reported in Table I.

TABLE I

Molecular parameters of  $^{17}\text{O}_2$  (in MHz)<sup>a</sup>

$B_0 = 40561.37(5)$	$\mu_1 = -0.000217(4)$
$\lambda_0 = 59498.879(5)$	$\alpha = -54.758(3)$
$\lambda_1 = 0.05479(4)$	$\beta = 46.679(3)$
$\mu_0 = -237.6462(9)$	$\chi = -8.29(5)$

a) Standard errors are given in brackets in the last digits quoted.

POPULATION INVERSION BETWEEN  $\Lambda$  DOUBLING  
LEVELS OF OH : EXPERIMENTAL EVIDENCE FOR  
THE INVERTING ROLE OF THE H - OH COLLISIONS

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The  $\Lambda$  doubling spectrum of OH in rotational ( $J < \frac{21}{2}$ ) and vibrational ( $v < 4$ ) levels has been observed in a cooled RF discharge in  $H_2-O_2$  mixture, leading to two types of results :

First, these new measurements allow us to improve the molecular parameters previously determined by COXON et al. [1].

Secondly, the population repartition within the  $\Lambda$  doublets in various rovibrational levels has been investigated versus the hydrogen concentration. At low hydrogen pressure, the lines always appear in absorption. When the hydrogen is in excess, the  $^2\Pi_{3/2}$  and  $^2\Pi_{1/2}$  levels behave differently : whereas the  $^2\Pi_{1/2}$  lines appear in absorption, the  $^2\Pi_{3/2}$  ( $0 < v < 4$ ) lines are seen in stimulated emission. In the best condition, the stimulated emission signals correspond to a gain of about  $5.10^{-7} \text{ cm}^{-1}$  and are readily seen in a 1 sec scan with a 3 ms lock-in time constant.

In order to elucidate the mechanism leading to this population inversion, other parameters such as total pressure, partial  $O_2$  pressure, electron density,  $H_\alpha$  emission have been simultaneously monitored.

Strong evidence for an excitation by H-OH collisions is found, as previously observed in other experimental conditions [2]. An approximate value for the rotational excitation rate constants can be derived.

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619 (1979).

[2] B. LEMOINE, R. BUSTREEL, C. DEMUYNCK-MARLIERE and J.L. DESTOMBES, J.  
Chem. Phys. 71, 3131 (1979).

INVERSE LAMB DIP SPECTROSCOPY USING MICROWAVE SIDEBANDS  
OF CO<sub>2</sub> LASER LINES

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A clear cut observation of infrared Lambdips using a  
widely tunable laser source is reported. The microwave  
sidebands generated on CO<sub>2</sub> laser lines provide sufficient  
power (~ 0.5 mW) and spectral purity (~ 100 kHz) for  
saturation spectroscopy. Infrared Lamb dip spectra of  
CH<sub>3</sub>F, NH<sub>3</sub>, SiH<sub>4</sub> and SiF<sub>4</sub> are presented.

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Diode Laser Spectroscopy of the  $\nu_3$  bands of  $\text{CF}_2$  and  $\text{NF}_2$

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The near prolate asymmetric rotor molecules  $\text{CF}_2$  and  $\text{NF}_2$  are both relatively long lived species which may be conveniently generated in the laboratory. In spite of this the  $\nu_3$  band centres and rotational parameters have not been reliably determined in the gas phase. In this study several hundred transitions in each  $\nu_3$  band were measured with a diode laser and assigned to derive accurate values for the band constants. The behaviour of both bands with respect to the matrix isolation studies is very similar and isotopic work is being pursued to determine their structure.

For  $\text{CF}_2$  the ground state constants are accurately known so that only the  $\nu_3 = 1$  rotational and centrifugal distortion constants and the band centre were varied to fit the data with an RMS error of  $0.0005 \text{ cm}^{-1}$ . Using a method based on the inertial defect the  $\nu_3 - \nu_1$  Coriolis coupling constant was independently determined. The microwave spectrum of  $\text{NF}_2$  however is relatively incomplete and so the ground state constants were redetermined including data from the  $\nu_3$  and  $\nu_1$  bands. The spin-orbit splitting in this a-type band is small compared to the b-type band and was well resolved only in the Q branch and a few of the R and P branch lines.

## High Resolution Spectrum of the $\nu_4$ Band of $\text{CD}_3\text{I}$

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The infrared spectrum of  $\text{CD}_3\text{I}$  has been recorded between 1830 and 2580  $\text{cm}^{-1}$  on the Fourier Transform Spectrometer at Laboratoire d'Infrarouge in Orsay. All the bands observed in this region,  $2\nu_2$ ,  $\nu_2 + \nu_5$ ,  $2\nu_5$ ,  $\nu_1$  and  $\nu_4$ , show effects of different perturbations.

In the  $\nu_4$  band between 2220 and 2390  $\text{cm}^{-1}$  we have assigned more than 2300 lines to sub-bands with  $K\Delta K$  from -18 to 21 including J values up to 70. At first sight the band, excepting  $R_{Q_8}$ , seems to be unperturbed. A more detailed investigation, however, reveals several perturbations. Altogether at least 8 different resonances can be detected. In the analysis we have included the interactions of  $\nu_4$  with four combination levels:  $\nu_3 + \nu_5^{\pm 1} + \nu_6^{\pm 1}$  ( $K\Delta K = 14$ ),  $\nu_2 + 2\nu_6^{\pm 2}$  ( $K\Delta K = 8, 9$ ),  $2\nu_3 + 2\nu_6^{\pm 2}$  ( $K\Delta K = -1, 0, +1$ ) and  $\nu_2 + 2\nu_6^0$  ( $K\Delta K = -11, -12$ ). All these interactions have been interpreted as Coriolis-type resonances and those sub-bands of  $\nu_4$  where the crossings have been observed are given in the parentheses. No interactions between the different combination levels have been included.

In the analysis we have constrained the ground state constants,  $A_0$  and  $D_0^K$  according to the results of Poulsen and Brodersen (J. Raman Spectrosc., in press). Part of the constants of the perturbing levels have also been fixed. Using 25 variable parameters a standard deviation of 0.0012  $\text{cm}^{-1}$  was obtained with 2132 lines.

Results for  $\nu_4$ :

$\nu_0$	$= 2298.54431(1) \text{ cm}^{-1}$	$D_0^J - D_4^J$	$= 0.65(2) \times 10^{-9} \text{ cm}^{-1}$
$\alpha_4^A$	$= 1.35021(9) \times 10^{-2} \text{ cm}^{-1}$	$D_0^{JK} - D_4^{JK}$	$= -7.8(4) \times 10^{-9} \text{ cm}^{-1}$
$\alpha_4^B$	$= 8.655(6) \times 10^{-5} \text{ cm}^{-1}$	$D_0^K - D_4^K$	$= 0.476(3) \times 10^{-6} \text{ cm}^{-1}$
$(\Lambda\zeta)_4$	$= 0.463800(3) \text{ cm}^{-1}$	$\eta_4^K$	$= 1.459(4) \times 10^{-5} \text{ cm}^{-1}$
$q_4$	$= 2.811(12) \times 10^{-5} \text{ cm}^{-1}$	$\eta_4^J$	$= -0.361(3) \times 10^{-5} \text{ cm}^{-1}$

## Diode Laser Spectroscopy with a Multiple Reflection Discharge Cell

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For the spectroscopy of unstable molecules we have constructed a White cell, consisting of three internal concave mirrors in confocal alignment, which allow multiple reflections of the diode laser beam, with a mirror spacing of 190 cm and a 10 cm diameter. This system has been used up to 52 traverses, totalling 99 m optical path length.

In using an absorption path of 46 m we found the lowest detectable molecule density to be  $6 \times 10^8$  molecules/cm<sup>3</sup>, for a S/N ratio between 1 and 2. This estimate was made from the S/N ratios of the absorption signals of both the fundamental lines R(21) and R(20) of OC<sup>34</sup>S and OC<sup>33</sup>S in their natural abundances and the lines R(40) and R(45) of the hot band  $11^1_0 - 01^1_0$  of OC<sup>32</sup>S and OC<sup>34</sup>S.

Furthermore the cell contains two stainless steel electrodes housed in two side branches of the cell spaced by about 180 cm. This system can be used for DC-discharges with a load resistance or -for regulation and modulation purposes - with a triode, which is connected to the cathode of the cell. The latter system has been used between 100 Hz and several kilo Hz. First test measurements were made on CO<sub>2</sub>, and is being applied towards the detection of unstable molecular species.

ANOMALOUS CENTRIFUGAL DISTORSION EFFECTS IN NON RIGID MOLECULES :  
THE WATER MOLECULE

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Because of the large amplitude motion of the hydrogen atoms, the water vapor molecule exhibits large centrifugal distortion effects. This leads to a poor convergence of the rotational hamiltonien when expanded as a series of the usual  $J_{\alpha}$  's. In particular, the expansion involves  $J_z^{2n}$  terms with high values of  $n$  (up to  $n = 7$ ). Alternative proposals are made to perform a partial resummation of this series leading to a satisfactory fit of the rotational levels of the ground state of  $H_2O$

LINE PROFILE IN THE INFRARED SPECTRUM OF N<sub>2</sub>O

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The evolution of the infrared absorption profiles of N<sub>2</sub>O under moderate pressures have been experimentally studied in the 2 μm region.

These experimental profiles are compared to those theoretically calculated under the following conditions :

- the short time correlation function of the dipole moment is calculated from a quasi-static theory for each line,
  - the longer time behaviour is calculated from impact theory including the finite duration of collision, also for each rotational line,
  - the intermediate time behaviour is deduced by an interpolating procedure,
  - the profile of any rotation-vibration line is computed by Fourier transforming the correlation function,
  - the resulting absorption profile is then calculated by summing all the lines absorbing significantly in the region under study.
-



PURE ROTATIONAL RAMAN SPECTRA OF ETHYLENE ISOTOPIC DERIVATIVES

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Work on band contour simulation of medium-resolution pure rotational Raman spectra of  $^{12}\text{C}_2\text{D}_2\text{H}_2$  and  $^{12}\text{C}_2\text{D}_3\text{H}$  will be presented. Our analysis aims the determination of relevant information about the molecular polarizability tensors, using energy constants and structural and force field data from the literature (1,2,3). This is considered as preliminary to further high-resolution studies on these same molecules.

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LABORATORY SPECTROSCOPY PROGRAMME AT RAL-

DESCRIPTION AND SOME INITIAL RESULTS

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A programme of laboratory spectroscopic studies in support of remotely sensed measurements of atmospheric composition will be described. Emphasis is being placed on the ability to make measurements of spectroscopic parameters under conditions of temperature and pressure which closely simulate those pertaining to the atmospheric measurements themselves.

The experimental facility comprises a high resolution interferometric spectrophotometer having a maximum unapodised resolution of  $0.002 \text{ cm}^{-1}$  at  $3000 \text{ cm}^{-1}$ , coupled to several absorption cells which give absorption path lengths from 5 cm to 1 km. All cells are operable over the temperature range 200k to 300k, can be used with high ( $> 5 \text{ bar}$ ) or low ( $< 10^{-5} \text{ torr}$ ) pressures of gas and are built of corrosion resistant materials. Measurements can be made on both pure absorber gas and on absorber gas/broadening gas mixtures. Path lengths from 32 m to 1 km are achieved in a modified White Cell which uses mirrors of 8 m radius of curvature and 12" diameter.

For analysing spectra, software is being developed to fit computer generated spectra to the experimental data, using the absorption line strengths and pressure broadened half widths as free parameters.

Preliminary spectra of a number of trace gases which play roles in the chemistry of the earth's atmosphere have been obtained. Results will be presented for the particular case of the HCl spectra around  $3.5\mu$  wavelength for which strengths and pressure broadened half widths have been obtained over the temperature range 200k to 300k.

\* This work is supported in part by the Chemical Manufacturers Association.

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Microwave spectra of excited states of cyclobutylsilane

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To the formerly reported spectra of axial and equatorial cyclobutylsilane which were assigned for the ground states and several excited states further spectra of excited states due to low lying vibrations of the equatorial conformer have been identified. Some obviously show perturbations.

DETERMINATION OF SPECTROSCOPIC CONSTANTS FOR THE  $A^2\Pi$  - STATE OF Na-AR BY LASER-SPECTROSCOPY

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The absorption spectrum of the transition  $X^2\Sigma^+ \rightarrow A^2\Pi$  of the van der Waals molecule sodium-argon has been investigated by means of laserspectroscopy using supersonic expansion through a nozzle into a vacuum for production of molecules. The experimentally observed lines could successfully be assigned to the rotational structure of vibrational bands with quantum numbers  $0 \leq v'' \leq 4$  and  $7 \leq v' \leq 11$ . For an accurate determination of the spectroscopic parameters of the excited  $A^2\Pi$  - state we used frequency differences between pairs of rotational transitions ending on the same level of the molecular ground state  $X^2\Sigma$ . The deviation from a pure Hund's case a for the  $A^2\Pi$  - state has been taken into account by diagonalizing the  $2 \times 2$  matrix of the molecular Hamiltonian between the  $^2\Pi_{1/2}$  and the  $^2\Pi_{3/2}$  state for given values of  $v'$  and  $J'$ .

In the  $\Pi_{3/2}$  - state we observed a small energy splitting between e- and f-levels allowing a direct determination of the A - type splitting parameter q. The corresponding experimental splitting in the  $\Pi_{1/2}$  - state could adequately be reproduced by replacing the usual A - type parameter p by the expression  $p + p_D J'(J'+1)$ . In addition to the parameters p,  $p_D$  and q of A - type doubling we have obtained values for the fine structure splitting parameters A and  $A_D$  and for the rotational parameters B and D for the vibrational states  $v' = 8, 9$  and 10.

A corresponding analysis has been performed for the molecular ground state  $X^2\Sigma$  [1] yielding a value of  $R_e = 5.008(5) \times 10^{-10}$  m for the equilibrium internuclear distance and of  $D_e = 41.7(8) \text{ cm}^{-1}$  for the well depth of this state.

[1] G. Aepfelbach, A. Nunnemann, D. Zimmermann  
Chem. Phys. Lett. 96 (1983) 311

*STRUCTURE OF KCN, NaCN, AND LiNC*  
*BY MOLECULAR BEAM ELECTRIC RESONANCE SPECTROSCOPY*

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The equilibrium geometries of gaseous KCN, NaCN, and LiNC have been the subject of numerous *ab initio* studies. These studies predict that these molecules are very floppy with zero-point bending motion amplitudes of up to  $15^\circ$ , and that the potential energy barrier in the bending direction is only marginal (less than 0.3 eV), yielding a "polytopic" bonding<sup>1</sup> for moderate vibrational excited molecules.

The molecular structures of the alkali metal cyanides are very sensitive to a subtle balance between a short-range and a long-range component of the interaction energy<sup>2</sup>. This leads to different effective structures in the ground vibrational state, which we determined experimentally to be T shaped for KCN<sup>3,4</sup> and NaCN<sup>5</sup>, and linear isocyanide for LiNC.

In this contribution we will present a summary of all the results on KCN, NaCN and LiNC which we obtained by molecular beam electric resonance spectroscopy. The emphasis will be on the latest results, being the determination of the structure of LiNC.

The LiNC molecule has been prepared by two totally different chemical reactions. We succeeded in producing a supersonic molecular beam (1% LiNC in Ar) using a tantalum double chamber oven. We measured two rotational transitions ( $J=1\rightarrow 0$  and  $J=2\rightarrow 1$ ) of <sup>7</sup>LiNC and one rotational transition ( $J=1\rightarrow 0$ ) of <sup>6</sup>LiNC in the ground vibrational state. The hyperfine structure was resolved and identified with the help of microwave-microwave double resonance. The rotational constants  $B_0$  and  $D_0$ , and the hyperfine coupling constants  $eQq(\text{Li})$ ,  $eQq(\text{N})$ , and  $c(\text{Li})$  have been determined for <sup>7</sup>LiNC. The rotational constant  $B_0$  of <sup>6</sup>LiNC could be deduced. We established that LiNC has a *linear* isocyanide structure. The results for the effective structural parameters are:  $r_{\text{LiN}} = 1.760 \text{ \AA}$ , and  $r_{\text{CN}} = 1.168 \text{ \AA}$ .

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LASER-STARK ANALYSIS OF THE  $\nu_2$  AND  $\nu_5$  BANDS OF  $\text{SiH}_3\text{F}$

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A study has been performed of the complex spectrum of  $\text{SiH}_3\text{F}$  in the region  $900\text{--}1050\text{ cm}^{-1}$ , where the  $\nu_2$  and  $\nu_5$  bands show a strong mixing by second order Coriolis coupling. The data under consideration consisted of over a thousand Stark resonances with  $^{12}\text{CO}_2$  and  $^{13}\text{CO}_2$  lasers, plus 13 new mm-wave measurements and around 900 infrared assignments from a Fourier Transform spectrum. The simultaneous use of different types of data has proved invaluable in the analysis, since the Laser-Stark spectra were often very dense and prone to misleading interpretation, and the very irregular infrared band contour was also difficult to interpret on its own. A step by step procedure has been followed where each type of data was used to check the progress in the analysis. In order to achieve a satisfactory final interpretation of the data, both the main Coriolis constant,  $\zeta_{25}$ , and those due to interactions with close vibrational states  $\nu_3=1$  and  $\nu_6=1$ ,  $\zeta_{35}$  and  $\zeta_{26}$ , have been included in the hamiltonian. The dipole moment, band origin and rotational constants of each vibrational state, and the  $B\zeta_{25}$  interaction constant, have been determined. Some Laser-Stark resonances have been identified of the  $^{29}\text{SiH}_3\text{F}$  species, allowing a fit of the  $\nu_5$  and  $B_5$  parameters of this molecule.

PERTURBATION AND PREDISSOCIATION EFFECTS IN THE  
 $A^3\Pi$  STATE OF THE  $SH^+$  AND  $SD^+$  IONS.

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We present the rotational analysis of the seven observed bands of  $SH^+$  and  $SD^+$   $A^3\Pi-X^3\Sigma^-$  transition, and the resulting molecular constants and potential energy curves. Semi-empirical and *ab initio* calculations of the spin-spin and spin-orbit contributions to the fine structure parameters are used to show that second-order spin-orbit interactions are responsible for the typical features of the  $SH^+$  X and A states : a) large ( $5\text{ cm}^{-1}$ ) spin doubling of the X state, ii) large  $\Lambda$ -doubling of the  $A^3\Pi_0$  component, iii) anomalous spin-orbit splitting of the A state. The first and second effects arise mainly from interaction with the  $b^1\Sigma^+$  state, while the third is due to the  $c^1\Pi$  state. Finally, the radiative and non radiative properties of the A state, are discussed in the framework of a crude quantum calculation of the predissociation rates for the lowest vibrational levels ( $v = 0-5$ ). The predissociation which does not show up in the  $v = 0$  level, is weak for  $v = 1$ , and is predicted to be very strong for  $v \geq 2$ .

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Vibrational-rotational analysis of the infrared  
fundamentals  $\nu_5, \nu_6, \nu_8$  and  $\nu_9$  of diazomethane

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Low pressure gas-phase infrared spectra of diazomethane,  $H_2CNN$ , have been recorded on a Digilab Fourier-transform spectrometer in the spectral range  $1200 - 450 \text{ cm}^{-1}$  at a resolution level  $0.06 \text{ cm}^{-1}$ . The K-type rotational structure of the c-type modes  $\nu_5$  and  $\nu_6$ , and the b-type modes  $\nu_8$  and  $\nu_9$  has been assigned.

A preliminary analysis is given for the strong a-type Coriolis interactions among these four modes. The rotational analysis is based on recent ground-state rotational constants from millimeter-wave studies (ref. 1.) and proceeds analogously to a treatment for similar perturbations in the ketene,  $H_2CCO$ , molecule (ref. 2) .

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## RADIATIVE LIFETIME MEASUREMENTS IN ION PAIR STATES OF I<sub>2</sub>

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In the 40,000 - 45,000 cm<sup>-1</sup> region, two ion pair states of I<sub>2</sub>  $1_g(^3P_2)$  and  $O_g^+(^3P_2)$  can be excited by optical double resonances via the B state. The radiative lifetimes of these two states have been measured as a function of the vibrational and rotational quantum numbers. For the two states, these lifetimes are not J-dependent. In the  $O_g^+$  state lifetime measurements over the range  $8 \leq v \leq 45$  exhibits a weak v-variation ; this measured lifetime is about 29 ns. In the  $1_g$  state, the lifetime has been measured for  $10 \leq v \leq 35$  and strong oscillations appear between the extreme values : 11 ns and 25 ns ; the period of these oscillations being about three vibrational quantum numbers.

Those very different lifetime behaviours between the two states are not surprising since the radiative relaxation mechanisms are different ; the fluorescence signal from the  $O_g^+$  state corresponds mainly to a transition towards the B state while the  $1_g$  state fluoresces mainly towards the A  $1_u$  state.

Various hypothesis can be proposed to interpret the lifetime oscillations in the  $1_g$  state. Calculations taking into account predissociation, perturbations or strong variation of the electric dipole moment as a function of the internuclear distance are now in progress.

OPTICAL-OPTICAL DOUBLE RESONANCE IN I<sub>2</sub> WITH AN U.V. CONTINUOUS WAVE LASER

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The O<sub>g</sub><sup>+</sup> (<sup>3</sup>P<sub>0</sub>) ion pair state of I<sub>2</sub> has been observed in the 53,000 - 54,000 cm<sup>-1</sup> region by optical-optical double resonance via the B state. The two step laser excitation is performed, first with a cw argon ion laser, second with a U.V. cw laser radiation delivered by a frequency doubled R6G ring dye laser.

Among the recent former observations of this state (1-4) the most extensive study is by J.C.D. Brand and A.R. Roy (4) who determined the spectroscopic constants up to v=25. Following a private communication this study has been extended up to v=60.

Our observations are relative to the 66 ≤ v ≤ 75 range, which allows more precise calculations of the spectroscopic constants.

Furthermore a perturbation affecting the v=70 level is clearly observed its interpretation is attempted by mixing with the O<sub>g</sub><sup>+</sup> (<sup>3</sup>P<sub>1</sub>) and 1<sub>g</sub> (<sup>3</sup>P<sub>1</sub>) states expected in this region ; thus, it would be the first experimental evidence for the existence of those not yet observed (<sup>3</sup>P<sub>1</sub>) states.

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## LASER EXCITED FLUORESCENCE SPECTRA OF

$^{39}\text{K}^6\text{Li}$  and  $^{39}\text{K}^7\text{Li}$

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Different lines of the argon ion laser and krypton ion laser have been used to excite spectra of  $^{39}\text{K}^6\text{Li}$  and  $^{39}\text{K}^7\text{Li}$  which have been measured photoelectrically with moderate resolution. In addition, a tunable dye laser, the newly designed injection heat pipe (IHP) [1] and a new technique, "selectively detected laser induced fluorescence" (SDLIF) [2] allow us to obtain a great amount of new information.

Recent work on  $\text{Na}^6\text{Li}$  and  $\text{Na}^7\text{Li}$  [3] has shown that their prominent visible absorption band system arises from transition  $B^1\Pi + X^2\Sigma^+$ . We have now examined the rotational structure of several bands of the B - X system of KLi, which lies in the region 5500 - 5900 Å. The bands were measured in excitation and in fluorescence. The large number of rotational levels populated and the overlap of different progressions makes LIF analysis difficult. Excitation spectroscopy, however, makes possible to pick out and resolve all P, R and Q lines, showing, in the case of unblended lines, the expected ratio of intensity. A-type doubling is small, so that the analysis includes R and P branches as well as Q branches in ten bands. An earlier vibrational analysis [4] is confirmed using band origins for both isotopic species and thus to determine the isotope shifts in both, the upper and the lower state. The results provide an unambiguous vibrational numbering.

The presence of a strong Q branch together with weaker P and R branches indicates that the transition is  $^1\Pi - ^1\Sigma^+$ . The fact that the system appears to be of normal intensity indicates an allowed transition: It is then most probably analogous to the  $B^1\Pi$  states of NaLi and NaK. There is very strong evidence that the states  $B^1\Pi$  of the mixed alkali dimers  $\text{MM}'$  are to be correlated with  $\text{M}(\text{ns}^2\text{S}) + \text{M}'(\text{np}^2\text{P})$ . The most reasonable assumption about the  $B^1\Pi$  state of KLi is that it is derived from  $\text{Li}(2\text{s}^2\text{S}) + \text{K}(4\text{p}^2\text{P})$ . Derived molecular constants and calculated RKR potential curves permit various calculations to be tested so that we can judge how reliable are present theoretical estimates [5].

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DOPPLER-FREE TWO PHOTON IONIZATION CROSSED LASER-MOLECULAR BEAM SPECTROSCOPY:

The  $K_2$   $B^1\Pi_u - X^1\Sigma_g^+$  band system

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The advent of the dye laser has brought major changes to high resolution optical spectroscopy of molecules. Their molecular constants which depend on spectroscopic measurements have been measured to orders of magnitude more accurately than was possible with the incoherent light source of pre-laser days.

In particular, molecular constants of alkali dimers, formerly measured to an accuracy of  $\sim 1$  part in  $10^5$  [1], are now quoted to few parts in  $10^7$ , largely through the work of Zare and coworkers [2,3], Demtröder et al. [4,5], Hessel et al. [6,7], and our own work [8-10]. Nevertheless, there is considerable room for improvement.

During the last year as a first step, to achieve higher accuracy, a molecular beam apparatus was made to work with a nozzle beam expansion of potassium, single photon LIF techniques and two photon ionization. The collimated supersonic nozzle beam of  $K_2$  molecules in the groundstate was crossed (a) with a tunable dye laser to excite fluorescence 12 cm downstream from the nozzle and (b) with the same tunable dye laser beam and an  $Ar^+$ -laser beam counter-propagating to excite and ionize the potassium dimer. The absorbed dye laser light excites to a given rovibronic level, whereas the  $Ar^+$ -laser line(s) do not excite or ionize potassium dimers from the ground state, but ionize excited potassium molecules with high efficiency. Thus, the  $K_2$   $B^1\Pi_u - X^1\Sigma_g^+$  band system has been observed with signal/noise ratios of  $> 200/1$  for LIF-detection and  $> 2000/1$  for ion-detection.

The rovibrational intervals have been measured to an accuracy of a few MHz ( $\sim 0.0001$   $cm^{-1}$ ). The result is that the level of analysis of molecular constants of  $K_2$  B - X is now relatively advanced to the order of magnitude of a few parts in  $10^9$ .

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COLLISION INDUCED TRANSITIONS IN ROTATIONAL MANIFOLD  
OF OCS PERTURBED BY Ar, He and H<sub>2</sub>

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We present results of infrared linewidth measurements at room temperature for OCS diluted in Ar, He and H<sub>2</sub> using a tunable diode laser in the 4.7 $\mu$ m spectral region. Information on the intermolecular potential is obtained and compared with results of semi-classical calculations by Liu and Marcus and IOS calculations of S. Green.

Pressure broadening data are compared to direct measurements of inelastic cross-sections by infrared double resonance.

How general is the concept of effective rotational hamiltonians for open-shell diatomics?

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In molecular spectroscopy, especially in the description and interpretation of high resolution spectra, an appropriate effective hamiltonian is used to fit the experimental data. This procedure yields for the electronic state under consideration molecular parameters, the precise physical nature of which is strongly dependent on the form of the effective hamiltonian.

In this paper we consider only the effective hamiltonian describing the rotational finestructure of open-shell diatomic molecules. For the analysis we choose an "appropriate" microscopic hamilton operator and a Born-Oppenheimer type basis set for a well specified Hund's coupling case. Using degenerate perturbation theory up to second order, which seems to be sufficient for our present purpose, a detailed calculation of the matrix elements yields the structure of the molecular parameters and the total energy as a function of the rotational and spin quantum numbers. The desired effective hamiltonian operating in the rotational subspace has to reproduce the same function for the energy.

We start in our work from a paper of Miller /1/, in which he investigated the finestructure of the  $^3\Pi$ -state of the hydrogen molecule. He defined molecular parameters which show an explicit dependence on the rotational quantum number. In our opinion this will not give a true effective hamiltonian.

Continuing this work our calculations indicate that it is not always possible to obtain a simple operator equivalent within the rotational subspace for the second order terms. This seems to become more severe for electronic states with angular momentum projection  $\Lambda \neq 0$ .

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Vibration-rotation spectra of OCS and CO<sub>2</sub> below 900 cm<sup>-1</sup>

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The regions of the  $\nu_1$  and  $\nu_2$  bands of OCS and of the  $\nu_2$  band of CO<sub>2</sub> were measured by the Fourier transform spectrometer in Oulu [1,2,3]. The resolution achieved was about 0.0045 cm<sup>-1</sup>. In addition to the fundamentals, many "hot" bands were observed and analyzed. The fundamentals of the less abundant isotopic molecules <sup>13</sup>C<sup>16</sup>O<sub>2</sub> and <sup>16</sup>O<sup>12</sup>C<sup>34</sup>S were observed, too. One of the goals of this work was to produce accurate wavelength standards for calibration use in high resolution infrared instruments. The second purpose was to improve the knowledge of some vibrational, rotational and centrifugal distortion constants of these molecules.

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GLYOXAL SPECTROSCOPY BY ENERGY LEVEL ANTICROSSINGS IN STRONG MAGNETIC  
FIELD

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Glyoxal molecule (CHO-CHO), carried by helium gas, is cooled in a supersonic jet ( $T_{rot} \sim 1$  K) ; its singlet rotational levels are excited by monomode, continuous, ring dye laser, locked on the fluorescence light of one of the glyoxal levels (blue).

The jet is located at the center of a SNCI's Bitter magnet coil producing a strong magnetic field  $B$  up to 8 Tesla with a homogeneity  $\delta B/B \sim 10^{-5}$  by  $cm^3$ . By the Zeeman effect, the magnetic field allows the coincidence of the triplet and singlet levels excited by the laser light. Singlet triplet couplings induce a 'level anticrossing'. The existence of anticrossing is governed by selection rules which may depend on the nature of the coupling Hamiltonian.

Anticrossing phenomena is observed on fluorescence light. The position in magnetic field of the anticrossings permits to determine the splittings between triplet rotational levels.

The accuracy of the measurement of the anticrossing position is limited by its width which depend on the coupling matrix element. The line width is at least equal to the natural line width : this is a sub-Doppler spectroscopic method.

Thus we have determined the rotational constant of several triplet vibrational levels about 2800 and 3500  $cm^{-1}$  above fundamental vibrational electronic state  $T_1$ . From these experiments we also obtained some singlet rotational constants which have never been measured before.

By a magnetic optical double resonance method we measured also fine and hyperfine structure of the triplet level. (The hyperfine structure is remarkably constant :  $83 \pm 3$  MHz on several hundreds of observed levels.)

The most important conclusion is that, in spite of such a high density of triplet vibrational levels ( $\sim 1$  level by  $cm^{-1}$  at 2800  $cm^{-1}$ ), triplet rotational state disposition is only weakly perturbed.

CO<sub>2</sub> LASER FREQUENCY STABILIZATION BY EXTERNAL DOPPLER DITHER  
MODULATION

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We have revived an idea first presented by M.W. Goldberg and R. Yusek<sup>1)</sup> for external Doppler dither modulation of CO<sub>2</sub> laser radiation. We applied this idea to the frequency stabilization of a CO<sub>2</sub> laser to the center of the 4.3- $\mu$ m fluorescence Lamb dip<sup>2)</sup> avoiding internal dither modulation of the laser frequency.

Part of the unmodulated CO<sub>2</sub> laser output is split by a partial reflector and is directed through a conventional fluorescence cell. Then it is focused onto a mirror moving back and forth along the optical axis of the laser beam. Thus, the frequency of the reflected laser beam is periodically Doppler shifted providing a first-derivative like fluorescence-radiation signal. Now the laser can be locked by a dc-servo loop to the center of the fluorescence Lamb dip.

The desired longitudinal movement of the mirror was obtained by a tuning-fork like device consisting of two steel blades ( $W \times H \times T = 7.5 \text{ mm} \times 40 \text{ mm} \times 0.2 \text{ mm}$ ) which were firmly connected at their ends to 4 mm thick spacers. If one end of this double-element tine is clamped to a heavy metal block, the mirror end is free to oscillate essentially along a straight line. The device was driven at its mechanical resonance ( $f = 173 \text{ Hz}$ ) by an ac electromagnet providing a frequency dither of up to  $\Delta f = \pm 900 \text{ kHz}$  on the reflected laser beam.

As the frequency modulation of the laser is accomplished outside the laser cavity, the laser's short term stability is not affected in contrast to conventional resonator-mirror dither schemes. This effect is shown comparing Lamb-dip spectra taken with externally (Doppler mirror) and internally frequency dithered CO<sub>2</sub> lasers.

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## SATURATION SPECTROSCOPY WITH A TUNABLE SIDEBAND LASER

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We report on the observation of saturation Lamb dips in the absorption spectra of  $\text{SiH}_4$ ,  $\text{SiF}_4$ ,  $\text{CH}_3\text{F}$ , and  $\text{NH}_3$  employing widely frequency tunable microwave-modulation sidebands of  $\text{CO}_2$  laser lines.

A few milliwatts of sideband radiation were generated by nonlinear frequency mixing of the 3-W output of a  $\text{CO}_2$  laser with about 20 W of microwave radiation within an electrooptic CdTe crystal of 50 mm length<sup>1)</sup>. The microwave signal was provided by a microwave frequency synthesizer and amplified by a TWTA within a frequency range of 12 - 18 GHz.

As the sideband frequency is given by the sum/difference of tabulated  $\text{CO}_2$ -laser and of synthesized microwave frequency, the absolute frequency scale in our spectra can be determined with an accuracy of about  $\pm 1$  part in  $10^9$ . A further advantage is the spectral purity of about  $\pm 2$  parts in  $10^{10}$  given by the short-term stability of our laser<sup>2)</sup> and by the residual FM of the microwave signal.

In this way, tunability, accuracy, and spectral purity so far associated only with  $\text{CO}_2$  waveguide laser spectroscopy<sup>3)</sup> can be extended over a substantially increased portion of the mid-infrared region.

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## TWO - PHOTON EXCITATION OF CO ( $A^1\pi$ )

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By a two photon transition, we have selectively excited CO in some rotational levels of the  $A^1\pi$ ,  $v=0$  state. This optical pumping experiment has been performed by frequency doubling a powerful pulsed dye laser. Some spectroscopic applications are here discussed. On the other hand, measurements of lifetimes have been achieved, which exhibit the influence of local perturbations of the  $A^1\pi$  state.

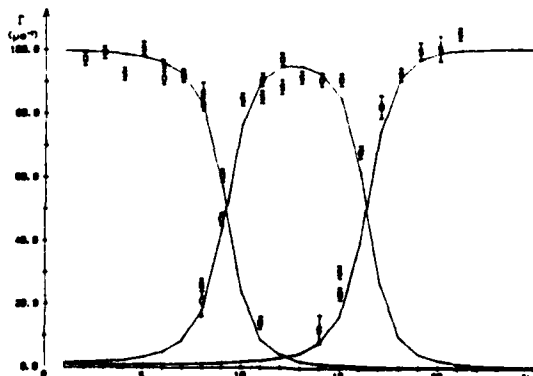
### 1) Spectroscopic results :

In order to calibrate the two-photon excitation lines of CO, a part of the visible beam (before frequency doubling) is used to record an  $I_2$  excitation spectrum. By this way, the CO excitation wave numbers (in the vacuum U.V.) are directly compared to the well known iodine excitation spectrum : a few measurements allow us to check the calibration of previous systematic spectroscopic data.

In another way, we have demonstrated the existence of important light-shifts (induced by a.c. Stark effect) in some usual experimental conditions : An symmetrical broadening of the lines of the CO two photon spectrum has been observed when using large power densities ; this effect is well interpreted by an inhomogeneous dynamical Stark effect and its order of magnitude agrees with theoretical calculations based on spectroscopic data : the  $A^1\pi$  state is shifted by coupling with some excited states ( $B^1\Sigma^+$  and  $C^1\Sigma^+$ ). Without zero power density extrapolation, such light-shifts can be a serious limitation to the multiphotonic spectroscopy.

### 2) Lifetime measurements :

Lifetimes of many rotational levels of both parities have been measured. We have observed strong variations of lifetimes near local perturbations of the  $A^1\pi$ ,  $v=0$  levels by the 3 components of the  $e^3\Sigma^-$ ,  $v=1$  state. Our results agree well with theoretical values deduced from spectroscopic data.



Fluorescence decay constants  $\Gamma_{rad}$  for some rotational levels  $A^1\Pi$  ( $v=0, J'$ ) and triplet-like states in the O and S branches (parity  $(-)^{J''}$ ). The continuous line refers to theoretical values deduced from Fink's calculations.

## THE EXCITATION SPECTROSCOPY OF CLUSTERS AND MOLECULES WITH AN INFRARED LASER

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Molecular clusters ( $\text{SiF}_4$ ,  $\text{SF}_6$ ,  $\text{C}_2\text{H}_4$ ,  $\text{CF}_3\text{Br}$  etc.) are produced in a supersonic beam which is crossed with a CW  $\text{CO}_2$ -laser. The absorption of a laser photon in the cluster produces dissociation and is detected as an attenuation of the beam-signal of the mass-spectrometer detector. The attenuation due to dimer dissociation was monitored upon the dimer- or monomer-ion mass-peak. Contrary to the infrared dimer induced vibrational bulk absorption spectra (e.g.  $\text{N}_2\text{-N}_2$ ), the dimer-excitation spectra in the frequency region of a molecular infrared active mode exhibit no individually resolved rotational lines. Typically the IR laser excitation spectrum consists of a single broad line. The occasional occurrence of two peaks for these spectra can be explained by resonant dipole-dipole forces between the molecular constituents. A puzzling feature of the excitation spectrum of a dimer is the shift of its line(s) center with respect to the frequency of the corresponding monomer vibrational mode of several  $\text{cm}^{-1}$ , distributed pseudo-randomly towards the red or blue. It will be shown that these shifts are related to Fermi-resonances with neighbouring vibrational levels, which resonance is enhanced (weakened) by the presence of the other constituent of the dimer (symmetry-breaker!).

In another experiment the vibrational excitation of an expanding  $\text{SF}_6$ -beam is investigated with a focussed CW  $\text{CO}_2$ -laser, employing the spontaneous Raman effect to monitor its vibrational state distribution. When the  $\text{CO}_2$ -laser interacts with a seeded  $\text{SF}_6$  beam (10% in He) at a rather large distance from the nozzle ( $x/D > 4$ ) the resulting excitation of the  $\text{SF}_6$ -molecules remains restricted to the vibrational levels of the pumped  $\nu_3$  mode only. The low rotational temperature of the  $\text{SF}_6$  molecules strongly impedes the collisionally induced transfer to other vibrational modes. The molecules are forced to climb the vibrational ladder of the resonant  $\nu_3$  mode.

A thermalized vibrational excitation among all modi results when the  $\text{CO}_2$ -laser impinges at a close distance from the nozzle ( $x/D \leq 1$ ). The higher rotational temperature and collision rate promote a fast redistribution of the energy absorbed. A maximum of 6 photons ( $T_{\text{vib}} = 950 \text{ K}$ ) could be stored into an  $\text{SF}_6$  molecule.

In yet another experiment strong visible luminescence was induced by our CW  $\text{CO}_2$ -laser after excitation of  $\text{CF}_3\text{Br}$  in bulk ( $p = 75 \text{ Torr}$ ,  $T = 300 \text{ K}$ ). Spectral analysis of the light showed that the radiance originates from  $\text{Br}_2^*$  apparently produced in a  $\text{CO}_2$ -laser induced pyrolysis of  $\text{CF}_3\text{Br}$ . High vibrational levels of  $\text{Br}_2^*$  are preferred as outcome of this process (population inversion?).

The frequency of the asymmetric rocking mode ( $\nu_g$ ) of ethylene has been investigated with the Raman effect.

ETUDE DU SPECTRE MICROONDE DU DICHLORODIFLUOROMETHANE

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Le spectre d'absorption de la molécule  $\text{CF}_2\text{Cl}_2$  du type toupie fortement asymétrique a été analysé de 12 à 160 GHz.

Deux spectromètres ont été utilisé :

- un spectromètre du type stark équipé d'une cellule d'absorption refroidie à  $-70^\circ\text{C}$

- un spectromètre du type vidéo équipé d'un détecteur superhétérodyne.

Les spectres relatifs aux formes isotopiques  $\text{C}^{35}\text{Cl}_2\text{F}_2$  et  $\text{C}^{35}\text{Cl}^{37}\text{ClF}_2$  ont été totalement indentifiés en ce qui concerne les états fondamentaux.<sup>2</sup> Cette analyse met en jeu des transitions concernant des valeurs élevées de J (70) et de K - 1 (50). Une étude de la structure hyperfine est réalisée. Les constantes moléculaires proposées incluent les termes de distorsion centrifuge ce qui permet de calculer de façon précise la totalité du spectre d'absorption.

VIBRATIONALLY INDUCED NUCLEAR QUADRUPOLE COUPLING IN THE  $\nu_3 = 1$   
STATE OF  $^{189}\text{OsO}_4$ .

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Electric nuclear quadrupole hyperfine structure arising from a nucleus at the center of tetrahedral molecules, such as  $^{189}\text{OsO}_4$ , is symmetry forbidden. However, in excited degenerate vibrational states, a small nuclear quadrupole coupling is induced. The hyperfine structure due to the vibrationally induced eqQ has been measured for a number of P- and R- transitions in the  $\nu_3$  fundamental of  $^{189}\text{OsO}_4$ , by using inverse Lamb dip spectroscopy. Microwave modulation side bands of  $\text{CO}_2$  laser lines have been used as the tunable infrared radiation. From the analysis of the observed hyperfine structure patterns the values of the scalar and tensor coupling constants,  $\chi_s^V$  and  $\chi_t^V$ , have been determined. Some high J levels in the  $\nu_3 = 1$  state of  $^{189}\text{OsO}_4$  appear strongly perturbed as a result of the mixing between the tetrahedral fine structure levels with the same symmetry, from different Coriolis sublevels. The shift of the perturbed levels and the corresponding variation of  $\chi_s^V$  and  $\chi_t^V$  are discussed.

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SPECTROSCOPIE A HAUTE RESOLUTION D'UN ION DIATOMIQUE SIMPLE  
ET DE SES ISOTOPES.

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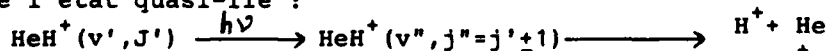
and

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RESUME

En accélérant des ions jusqu'à une énergie cinétique de l'ordre du keV, on réduit leur distribution de vitesse à quelques m/s et on s'affranchit ainsi de l'élargissement Doppler. En configuration faisceau d'ions parallèle ou anti-parallèle à un faisceau laser de fréquence fixe, on accorde par effet Doppler la fréquence sur une transition entre états moléculaires en faisant varier l'énergie cinétique des ions.

Les transitions entre états liés et quasi-liés de l'ion moléculaire  $\text{HeH}^+$ , par exemple, sont caractérisées par la détection des fragments  $\text{H}^+$  provenant de la prédissociation rotationnelle de l'état quasi-lié :



Les différentes combinaisons isotopiques de  $\text{HeH}^+$  ont été étudiées:  $^4\text{HeH}^+$ ,  $^4\text{HeD}^+$ ,  $^3\text{HeH}^+$ ,  $^3\text{HeD}^+$ , tant sur le plan expérimental que théorique. Au total 10 transitions et largeurs d'états quasi-liés ont pu être comparées. Les prévisions des calculs théoriques (à  $0.2 \text{ cm}^{-1}$  près) ont permis d'identifier les transitions expérimentales mesurées avec une précision de  $0.02 \text{ cm}^{-1}$ , une amélioration de cet accord implique le calcul des corrections non-adiabatiques.

D'autre part, un effet non totalement expliqué concerne l'évolution du profil de la raie qui caractérise l'état quasi-lié, en fonction de la puissance du laser.



LOCAL MODE CHARACTER IN THE (2000) STRETCHING OVERTONE BAND OF GERMANE

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The region containing the first overtones of the GeH stretching vibrations of germane has been examined at Doppler-limited resolution with a difference-frequency laser spectrometer. Only one of the two possible  $F_2$  components has been located, giving rise to a fairly strong band close to  $4155\text{ cm}^{-1}$ . Searches for the second component revealed only very weak lines with no obvious pattern. The  $F_2$  component observed is strongly perturbed by an  $A_1$  component lying less than  $0.4\text{ cm}^{-1}$  below the  $F_2$  band origin. The  $F_2$ - $A_1$  closely-coupled pair of bands has been analysed in detail for all five isotopic species of germane. An isotopically-enriched sample of  $^{74}\text{GeH}_4$  was studied, allowing transitions up to  $J' = 20$  to be assigned; for this species, a fourth-order Hamiltonian has been used to fit over 1000 assignments with a standard deviation better than  $0.0003\text{ cm}^{-1}$ . Improved values of the scalar ground state constants have been determined. The species  $^{70}\text{GeH}_4$ ,  $^{72}\text{GeH}_4$ ,  $^{73}\text{GeH}_4$ , and  $^{76}\text{GeH}_4$  have been studied only in a natural isotopic mixture, permitting their spectra to be assigned only to  $J' = 12$ . Molecular constants will be presented, and the vibrational nature of the bands will be discussed in relation to local mode theories.

FTIR Spectra of Various Isotopic Species of Methyleneimine

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We shall present results on the observation and analysis of FTIR spectra of methyleneimine  $\text{CH}_2 = \text{NH}$  in various isotopic forms ( $\text{H/D}$  and  $^{14}\text{N}/^{15}\text{N}$ ). The spectra were taken on the Nicolet 7199 FTIR system at Reading, supplemented by data obtained on the higher resolution Kitt Peak FTIR system, and by data obtained by laser Stark spectroscopy at Bristol and at Strathclyde Universities.

SUPERHYPERFINE STRUCTURES IN THE  $\nu_3$  BAND OF  $SF_6$

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The clustering of lines in the fine structure of the infrared spectra of spherical-top molecules leads to situations where vibration-rotation splittings within clusters (superfine structure) are negligible compared to the hyperfine splittings (1). These situations occur especially for high  $J$ - values and towards the ends of each  $J$  manifold and are called superhyperfine structures. A dozen of such structures have been observed (2) for the first time, in the  $\nu_3$  band of  $SF_6$ , for various cases of threefold and fourfold clusters. The theoretical spectra calculated with the spin-rotation, spin-vibration and spin-spin interactions, as described in previous works (3), are in excellent agreement and will be displayed. We shall also analyse, through nomograms, a few intermediate cases where the superfine splittings are very small but not negligible.

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