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British Radiofrequency Spectroscopy Group

Spring Meeting 1984

'MICROWAVE and FAR INFRARED SPECTROSCOPY
of TRANSIENT MOLECULES'



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University of Cambridge

Department of Chemistry

Acknowledgements

The British Radiofrequency Spectroscopy Group gratefully acknowledge financial support from the following organisations:

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Conference Organizer -
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University of Cambridge,
Lensfield Road,
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Conference Programme

The Scientific Sessions will start at 14.15 hours on Monday April 9th and end at 12.45 hours on Wednesday April 11th. They will be held in Lecture Theatre 2 at the Chemistry Department in Lensfield Road.

Posters

Posters should be mounted on Monday morning on the first floor foyer outside Lecture Theatre 1 (see map of the department). Members of the organising committee will be on hand to help and will have a supply of adhesive material available.

Registration

The Registration Desk is situated outside Lecture Theatre 2 and will be open on Monday morning from 10.00 hours. When closed messages may be left with the receptionist (telephonist) in the foyer.

Refreshments

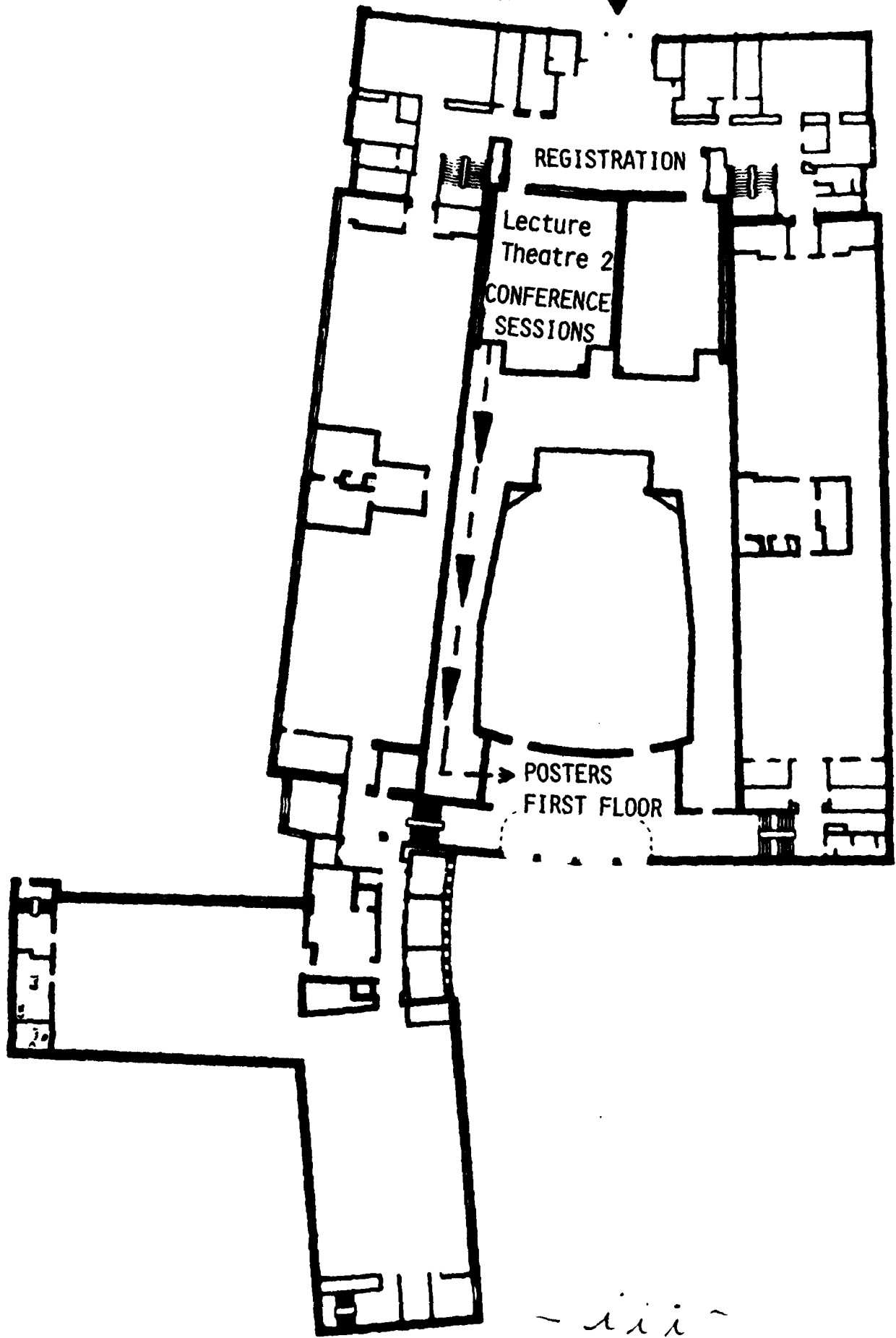
Tea and coffee will be served in the registration area.

Visits to Laboratories

Visits to groups in the Department of Physical Chemistry will be arranged after lunch on 11th April as required.

CAR PARK

MAIN ENTRANCE



Lensfield Road

→ Partial Contents :

PROGRAMME

Sunday 8th April:

7.00 p.m. DINNER (EMMANUEL COLLEGE)

Monday 9th April:

8.00 a.m. - 9.00 a.m. - BREAKFAST

From 10.a.m.

REGISTRATION : DEPARTMENT OF PHYSICAL CHEMISTRY

1.00 p.m. LUNCH

→ MOLECULAR BEAM SPECTROSCOPY ;

2.15 p.m. Opening Remarks : B. Bleaney

2.20 p.m. D-Nuclear Quadrupole Coupling in Weakly Bound Dimers -
from Pulsed-Nozzle, Fourier Transform Microwave
Spectroscopy ;

A.C. Legon

3.10 p.m. Spectroscopy of Radicals in Molecular Beams ;

W.L. Meerts

4.00 p.m. TEA

4.30 p.m. Electric Dipole Moments of Alkaline Earth Monohalides ;

T. Törring, W.E. Ernst and S. Kindt

7.00 p.m. DINNER

next page →

Tuesday 10th April: 8.00 a.m. - 9.00 a.m. - BREAKFAST

MICROWAVE SPECTROSCOPY OF FREE RADICALS AND IONS

Chairman : D.H. Whiffen

9.15 a.m. → Millimeter and Submillimeter Studies of Free Radicals
and Molecular Ions

F.C. De Lucia

10.05 a.m. → Microwave Studies of Molecules of Chemical, Theoretical
and Astrophysical Interest

H. Kroto

10.55 a.m. COFFEE

11.15 a.m. → High Resolution Spectroscopy and Structure of XO_2 ,
 XSO and CH_2X Molecules

E. Hirota

12.05 p.m. → The Rotational Energy Levels of CH , SiH and GeH

J.M. Brown

1.00 p.m. LUNCH

FAR INFRARED LASER MAGNETIC RESONANCE

Chairman : B.A. Thrush

2.20 p.m. "Far Infrared Laser Magnetic Resonance"

K.M. Evenson

3.10 p.m. "Far Infrared Laser Magnetic Resonance Spectrum of the
 AsH Radical in its $X^3\Sigma^-$ state"

K. Kawaguchi and E. Hirota

3.25 p.m. "New FIR Laser Magnetic Resonance Spectra of Diatomic
and Polyatomic Radicals"

J.R. Anaconda, P.B. Davies, A.H. Ferguson and F. Temps

- 4.00 p.m. TEA
- 4.30 p.m. POSTERS
- 6.15 p.m. RECEPTION - OLD LIBRARY, EMMANUEL COLLEGE
- 7.00 p.m. DINNER

Wednesday 11th April: 8.00 a.m. - 9.00 a.m. - BREAKFAST

NEW TECHNIQUES AND FREQUENCY MEASUREMENT

Chairman : A.D. Buckingham

- 9.15 a.m. "Tunable Far Infrared Laser Spectroscopy"
K.M. Evenson
- 10.05 a.m. "Frequency Measurement Techniques and Lasers in the
Far Infrared"
D.J.E. Knight
- 10.55 a.m. COFFEE
- 11.15 a.m. "Proposed New Method for Radiofrequency Spectroscopy
of Molecular Ions"
D.K. Russell
- 11.45 a.m. "Spectroscopy of Muonium-Substituted Organic Radicals"
S.F.J. Cox
- 1.00 p.m. LUNCH AND DEPARTURE

POSTER SESSION 4.30-6.30 TUESDAY 9th APRIL

1. "Millimetre Wave Spectrum of the ^{13}C N Free Radical"
M. Bogey, C. Demuyne and J.L. Destombes
2. "Millimeter and Submillimeter Wave Spectrum of Oxygen in the $a^1\Delta_g$ State"
G. Cazzoli, C. Degli Esposti and P.G. Favero
3. "The Millimeter Wave Spectrum of Methyl Hydroperoxide (CH_3OOH)"
C.E. Blom
4. "Microwave and Millimeter Wave Spectrum of ^{13}C -Diazirine H_2CN_2 :
Rotational and Hyperfine Structure Analysis"
K. Möller, J. Vogt and M. Winnewisser
5. "Far Infrared Magnetic Resonances in Pulsed Magnetic Fields"
P. de Groot, P. Janssen, F. Herlach, G.De Vos and J. Witters
6. "New Far Infrared LMR Spectra of Sulphur Radicals"
J.R. Anacona and P.B. Davies
7. "Relative Stability and Equilibrium Geometries for some HAB Systems"
P.J. Bruna
8. "EPR at FIR Frequencies in TmVO_4 and DAG"
P. Janssen
9. "Ab Initio Study of the $^2\Pi_1$ State of OH : Spin-Orbit Splitting,
 Λ -Doubling and Einstein Coefficients"
R. de Vivie, R. Klotz, C.M. Martin and S.D. Peyerimhoff
10. "Low-Lying Electronic States and Franck-Condon Factors for SiN , SiP ,
 P_2^+ , Si_2^- , CSi^- , SiP^+ and SiN^+ according to MRD-CI Calculations"
V. Krumbach, H. Dohmann, J. Anglada, P.J. Bruna and S.D. Peyerimhoff
11. "Ab initio calculation of the CH^+ ion near its dissociation limits.
R. Klotz, C.M. Marian and S.D. Peyerimhoff."

D-nuclear quadrupole coupling in weakly bound dimers
from pulsed-nozzle, Fourier-transform microwave spectroscopy

A.C. Legon

This contribution will be concerned with the technique of pulsed-nozzle, Fourier-transform microwave spectroscopy conducted in a Fabry-Perot cavity and its application to the investigation of weakly bound dimers of the type $B \cdots HA$ through their rotational spectra. A brief description of the technique, in which particular emphasis will be given to its sensitivity for weakly bound dimers and its resolution, will be followed by an account of results obtained from the analysis of D-nuclear quadrupole and H, ^{19}F nuclear spin-nuclear spin hyperfine structure in a number of dimers $B \cdots HA$ and $B \cdots DA$, where B is, e.g., HCN, H_2O , H_2S and HA is, e.g., H(D)F or H(D)CN. Some conclusions about changes in the HA molecules that accompany formation of the dimer will be presented.

SPECTROSCOPY OF RADICALS IN MOLECULAR BEAMS

W. Leo Meerts

In the present paper several different methods to study radicals in molecular beams will be discussed: the molecular beam electric resonance technique (MBER) and two different microwave-optical double resonance experiments.

The MBER technique features high sensitivity and very high resolution. The latter being one of the main advantages of the use of molecular beams in spectroscopy. Due to its high resolution fine structure such as Λ -doubling and hyperfine structure could be studied with high accuracy. This has been done in the past for NO, OH, SH and several isotopic species. In addition the molecules can be studied in the presence of external electric and magnetic fields. The Stark splittings yield the electric dipole moment with an accuracy of 1 part in 10^4 , while the Zeeman experiments are particularly applicable in the essential non-paramagnetic $^2\Pi_{1/2}$ states. Combination of the results of the latter experiments with those on the paramagnetic $^2\Pi_{3/2}$ states allows a complete determination of the g-factors in a $^2\Pi$ state and the molecular quadrupole moment. Results are obtained for NO and experiments are presently carried out on OH.

One of the main drawbacks in the study of radicals with molecular beams is the low radical concentration and therefore problems with sensitivity arise rather quickly. This problem has been overcome by combining the high resolution attainable in a molecular beam with the high sensitivity of the detection by means of optical photons. Two different microwave-optical double resonance schemes have been applied, both using single frequency optical lasers. In the first scheme a state selected molecular beam is detected by laser induced fluorescence and the microwave transitions are induced in the ground electronic states. The detection and microwave transition regions are spatially separated. The $A^2\Pi_{3/2} + X^2\Pi_{3/2}$ system of the IO radical has been studied¹⁾ as an example. In the second method the molecular beam is crossed at two points by a split laser beam. The first intersection is used to induce the microwave-optical double resonance, while the second intersection is used to detect this double resonance by laser induced fluorescence. In this way the ρ -doubling in the excited $A^2\Sigma^+_{1/2}$ state of OH was studied²⁾ under high resolution.

A brief description of the various methods and results will be presented.

1) J.P. Bekooy, W.L. Meerts and A. Dymanus
J. Mol. Spectrosc. 102 (1983) 320

2) J.J. ter Meulen, W. Ubachs and A. Dymanus
Laser Spectroscopy VI, 345 (1983), Ed. H.P. Weber and W. Lüthy

Electric Dipole Moments of Alkaline Earth Monohalides

T. Törring, W.E. Ernst and S. Kindt

Precise values for the electric dipole moments of CaCl, CaBr /1, 2/ and CaF /3/ have recently been determined from molecular beam resonance experiments. The results are in complete disagreement with predictions from the Rittner model /4/. A modification of this simple electrostatic model is discussed which takes into account explicitly the large charge shift of the unpaired valence electron resulting from the polarization of the Me^+ ion. It is shown that this improved model leads to good agreement not only with experimentally determined dipole moments but also with spectroscopic constants α_e , $\omega_e x_e$ and D_i for all alkaline earth monohalides investigated so far.

/1/ W.E. Ernst, S. Kindt and T. Törring
Phys.Rev.Lett. 51 979 (1983)

/2/ S. Kindt, W.E. Ernst and T. Törring
Chem.Phys.Lett. , 103, 241 (1183)

/3/ W.J. Childs, L.S. Goodman, K. Nielsen and V. Pfeifer,
private communication

/4/ E.S. Rittner
J.Chem.Phys. 19, 1030 (1951)

MILLIMETER AND SUBMILLIMETER STUDIES OF
FREE RADICALS AND MOLECULAR IONS

F.C. De Lucia

We have recently developed a technique for the enhancement of positive molecular ion concentrations in glow discharges. The technique consists of modifying an anomalous glow discharge by the addition of a longitudinal magnetic field of up to 300 G. Enhancements in the ion signal strength are approximately two orders of magnitude and are ion specific. Diagnostic experiments indicate that the magnetic field increases the length of the ion rich negative glow by restricting inside a small diameter tube the ionizing electrons accelerated by the large cathode drop of an anomalous glow discharge. This system has been used to study a number of positive ions including trace isotopic species in natural abundance. Recent work on several free radicals will also be discussed.

Microwave Studies of Molecules of Chemical, Theoretical
and Astrophysical Interest

Harold Kroto

Microwave spectroscopy has been used to detect and firmly identify various new unstable molecules. The molecules have, in general, derived their instability from the reactivity of multiply bonded groups they contain. The studies have provided vital information on synthetic methods in addition to the usual structural and vibration-rotation data. It is this chemical aspect of the microwave experiments that has unlocked other areas of study. In addition to complementary spectroscopic information using photoelectron and infra red techniques the value of the molecules as chemical intermediates and ligands has also been explored. Some of these molecules have been detected in the interstellar medium and the microwave spectra of various related molecules are now being studied for radio search experiments in order to shed light on the processes by which large molecules are formed in space.

High Resolution Spectroscopy and Structure of XO_2 , XSO ,
and CH_2X Molecules

Eizi Hirota

The present talk will be divided into two parts; one part will be devoted to the structures and force fields determined for non-linear XYZ-type molecules and the second part will focus attention primarily to the planarity of CH_3 and its derivatives.

1. Equilibrium Structures and Anharmonic Potential Constants of XO_2 , XSO , and Related Molecules.

High resolution spectroscopic data reported for HO_2 , HCO , HNO , and their deuterated species not only in the ground vibrational states, but also in excited vibrational states allow us to determine the equilibrium structure and force field including third-order anharmonic potential constants for these molecules. The same method has also been applied to a few non-linear XYZ-type molecules which are more or less related to the three parent molecules, although much less complete information has been obtained for these molecules. In this way we were able to estimate the molecular structures of HPO and FCO_2 for which the rotational constants have so far been determined only for the parent species.

2. Molecular Structures of CH_2X -type Molecules

As Walsh diagram indicates, the planarity of CH_3 and its derivatives is very difficult to predict. In fact, three recent examples do show the variety of molecular structures: CH_3 planar with an out-of-plane bending potential of large quartic nature, CF_3 pyramidal with the FCF angle of $110.7_6 \pm 0.4^\circ$, and CH_2F almost planar with the low-frequency (300cm^{-1}) out-of-plane bending mode. We have recently investigated two related molecules, CH_2Cl and CH_2CHO . The CH_2Cl radical is planar, as expected from smaller electronegativity of Cl than F. The second molecule, the vinoxy radical, has been known as an important intermediate in hydrocarbon reactions. We have confirmed that it exists mainly in the $CH_2-CH=O$ resonance form and is planar.

The Rotational Energy Levels of CH, SiH and GeH

J. M. Brown

Measurements of microwave frequencies in the free radicals CH and SiH by microwave-optical double resonance will be described. Such frequencies provide information on the lambda-doubling intervals and the proton hyperfine structure; they are also of astrophysical interest. This work is prefaced by measurements in the far infrared by LMR on these radicals. Related work on the GeH radical will also be presented.

LASER MAGNETIC RESONANCE SPECTROSCOPY OF ATOMS

K.M. Evenson

Far infrared Laser Magnetic Resonance spectroscopy is applied to fine structures of atoms. The accuracy and sensitivity of the technique, combined with the accuracy of the Zeeman theory of atoms, allow precise determination of frequency intervals and g_j factors. The recent measurements of the metastable $^3p_0 \rightarrow ^3p_1$ transition in magnesium and the $^3p_0 \rightarrow ^3p_1$ transitions in silicon will be described. The atomic silicon measurements are the most accurate ever made by laser magnetic resonance.

Far-Infrared Laser Magnetic Resonance Spectrum

of the AsH Radical in $X^3\Sigma^-$

Kentarou Kawaguchi and Eizi Hirota

Five rotational transitions of AsH were observed using five optically-pumped CH_3OH , CH_3OD , and CH_2F_2 laser lines as sources. The radical was generated by the reaction of metallic arsenic with microwave discharge products of a H_2/O_2 mixture. From an analysis of the observed spectrum, the following molecular constants were obtained:

$B_0 = 215\,877.54(23)$, $D_0 = 9.834(11)$, $\lambda = 1\,763\,488(56)$,
 $\gamma = -8114.5(60)$, $\alpha_{\text{As}} = -11.5(14)$, $\beta_{\text{As}} = -159.4(13)$,
 $eQq_{\text{As}} = -97.6(72)$, $\alpha_{\text{H}} = -49.80(66)$, and $\beta_{\text{H}} = 4.15(60)$,
all in MHz with 3σ in parentheses. The molecular and electronic structures of AsH will be briefly discussed using the observed molecular constants.

New FIR Laser Magnetic Resonance Spectra of Diatomic and Polyatomic Radicals.

J.R. Anaconda, P.B. Davies, A.H. Ferguson and F. Temps

Several new LMR spectra have recently been detected using both optically pumped and discharge excited FIR laser sources. Earlier work on $\text{NF}^1\Delta$ has been extended to four rotational transitions of the ground vibrational state between $J = 5$ to 13. Improved sensitivity has yielded spectra from $V = 1$ assignable to $J = 6 \rightarrow 7$ and $8 \rightarrow 9$. The results are compared with those from diode laser spectroscopy of the fundamental band of $^1\Delta\text{NF}$. Finally a spectrum of $699\mu\text{m}$ has been tentatively assigned to a rotational transition in $V = 2$.

Spectra of two rotational transitions of the $^{14}\text{N}^{32}\text{S}$ radical have been detected using discharges in N_2 and SCl_2 to generate this species. The Zeeman patterns form classic LMR spectra of a diatomic $^2\Pi$ radical. The feature of particular interest is the Λ doubling in the $^2\Pi_{3/2}$ state which is too small to resolve in the lower rotational levels. More details are given in Poster P6. In contrast much more complicated spectra from a polyatomic radical have been detected at $108\mu\text{m}$ using a D_2O discharge laser. The most likely carrier of the spectrum is the previously unobserved HCS radical but at this stage CH_3S cannot be excluded.

TuFIRS: TUNABLE FAR INFRARED LASER SPECTROSCOPY

K.M. Evenson

The non-linear Tungsten-Nickel point contact diode has been used to provide tunable far infrared radiation from the difference frequency of two CO lasers.

This is the first demonstration of tunable CW FIR radiation promising complete coverage of the region from 0.1 to 5THZ.

The technique of generating the radiation using the diode will be described. Rotational spectra of CO, HF, and HNO₃ have been observed using this new source and will be described.

Frequency-measurement techniques and lasers in the far-infrared

D.J.E. Knight

A brief description of the techniques of laser frequency measurement will be followed by discussion of some items concerned with laser frequency measurement at NPL. Two far-infrared lasers are used at 70.5 μm and 215 μm as part of a harmonic multiplication chain to reach a frequency standard in the visible spectral region. Both are needed to reach a specific CO_2 laser line, the 9.22 μm R(30) line at 32.5 THz, and their frequencies must be measured using microwave harmonics, themselves measurable against the caesium standard. Also a 187 μm line in CH_3F has been measured recently, in collaboration with P B Davies et al. of Cambridge.

In the Division of Electrical Science, a compact optically-pumped laser system having a waveguide CO_2 pump laser and a waveguide far infrared cavity has been investigated; also work continues on the evolution of Josephson devices for frequency mixing and heterodyne detection, towards more compact cryostats and possible thin -film junctions.

The NPL list of cw far-infrared laser lines was last revised in 1980-81, although reprinted with an added pump-ordered list in 1982. This has 1350 lines from 62 gases. About 1100 new lines and 20 new lasing gases have since been reported. The availability of far-infrared sources, especially of powerful ones will be discussed.

Proposed New Method for Radiofrequency Spectroscopy of Molecular Ions.

D.K. Russell

A method is proposed whereby low frequency spectroscopic transitions in molecular ions may be detected. The ions are trapped in a combination of electric and magnetic fields and exposed to an inhomogeneous field at the sum frequency of ionic motion in the trap and a transition of the ion. The resulting motion of the ions may be detected via the image charges induced in capacitor plates containing the ions. Numerical examples are given.

Spectroscopy of muonium-substituted organic radicals

S.F.J. Cox

Short lived muonium-substituted radicals are formed when positive muons are implanted in unsaturated organic materials. Information on their physical and chemical properties, equivalent to that provided by ESR and ENDOR, may be obtained by the technique which has become known as Muon Spin Rotation, or μ SR.

Comparison of the hyperfine interaction constants of the muonic radicals with that of their "normal" or protonic counterparts reveals large isotope effects which may be interpreted in terms of the conformation and internal dynamics of the molecules. Values may be extracted for the energy barriers to rotation or vibration for the muonium-labelled groups within species of high molecular weight.

The sensitivity and timescale of the μ SR techniques combine to permit fast processes and transient species to be monitored by various methods over a total range 10^{-12} - 10^{-4} s. Direct rate measurements of reaction or conversion of the muonic species are possible in the range 10^{-7} - 10^{-5} s. In radiation chemistry, μ SR has the unique property that it allows observation not only of certain products of the radiolysis, but follows the history of the ionising particle itself.

Experimental results from groups working at CERN (Geneva), SIN (Zürich) and TRIUMF (Vancouver) illustrate these principles.

MILLIMETER WAVE SPECTRUM OF THE ¹³CN FREE RADICALM. BOGEY, C. DEMUYNCK and J.L. DESTOMBES

The microwave spectrum of the ¹³CN free radical is observed in a R.F. glow discharge.

The hyperfine structure of the $N = 0 \rightarrow 1$ and $1 \rightarrow 2$ transitions in excited vibrational states ($v < 4$) is analyzed, leading to a good determination of the fine and hyperfine structure molecular constants. Comparison with the isoelectronic CO^+ molecule is made, and breakdown of the Born-Oppenheimer approximation is considered.

P2 Millimeter and submillimeter wave spectrum of oxygen in the a ¹Δ_g state.

G. Cazzoli, C. Degli Esposti and P.G. Favero

The measurements of two rotational transitions of oxygen in the a ¹Δ_g electronically excited state in the millimeter and submillimeter wave region allowed a more accurate determination of the molecular parameters of this molecule. The newly determined values in MHz are : B₀ = 42504.523 (4), D₀ = 0.1526 (1);
q = 7.8(55) x 10⁻⁵

The millimeterwave spectrum of
methyl hydroperoxide (CH₃OOH)

C.E. Blom

Recently, the microwave spectrum of methyl hydroperoxide between 12.5 and 60 GHz has been reported (1). The energy difference between the lowest vibrational states, O^+ and O^- , was estimated to be around 15 cm^{-1} .

In order to determine an accurate Hamiltonian for CH_3OOH we are presently investigating the millimeter- and submillimeterwave spectrum. Results for the region between 100 and 300 GHz will be presented.

- (1) M. Tyblewski, R. Meyer and A. Bauder, presented at the 8th Colloquium on High Resolution Molecular Spectroscopy, Tours, 1983, paper H13.

P4 Microwave and Millimeter Wave Spectrum of ^{13}C -Diazirine, H_2CN_2 :
Rotational and Hyperfine Structure Analysis

Klaus Möller, Jürgen Vogt and Manfred Winnewisser

Diazirine is the only stable three-membered ring isomer of diazomethane. It does not decompose in the gaseous phase, but can explode in the condensed states. The rotational spectrum of ^{13}C -enriched diazirine has been measured in the microwave and millimeter wave region up to 250 GHz. The a-type R- and Q-branch transitions have been assigned for the ground vibrational state. A centrifugal distortion analysis has been carried out using the A-reduced Watsonian. As in the main isotopic species the effects of nuclear quadrupolar and spin-rotational interactions lead to a characteristic hyperfine structure of the individual transitions which was analysed in order to determine the appropriate quadrupolar and spin rotational constants. The constants which will be reported reproduce the observed experimental spectrum. The spectroscopic constants obtained by a least squares fit are currently being used in the analysis of the high resolution infrared spectrum of ^{13}C -diazirine.

P. De Groot, P. Janssen, F. Herlach, G. De Vos and J. Witters

In our laboratory we have developed an EPR spectrometer capable of detecting $g = 2$ resonances at frequencies up to 10^{12} Hz (wavelength 0,3 mm). The radiation source consists of either an HCN laser or a far infrared laser with a CO_2 pump. The magnetic field is generated in a pulsed coil powered by a condenser battery. The maximum field without coil destruction is 40 Tesla and the pulse duration is about 10^{-2} s. The spectra that we have investigated up to now are 1) transmission spectra of two kinds of samples : thick transparent spherical crystals of Li-rare earth - F_4 , and thin transparent plates of $(\text{CH}_3)_4\text{NMnCl}_3$ (TMMC), and 2) strip-line spectra of ferromagnetic thin films of Ni. The transmission spectra are complicated because of reflection effects in the regions where the permeability becomes negative and also because of magnetostatic modes in the sample. It is possible however to use rather simple analytical solutions of Maxwell's and Bloch's equation to analyse the spectra and to extract the relevant parameters. The most significant results are the temperature - and field dependence of the TMMC resonance line, which can be tentatively explained by the concept of thermal excitation of solitons and the large linewidth (about 5 T.) of the Ni resonance for which no explanation is available.

New Far Infrared LMR Spectra of Sulphur RadicalsJ.R. Anacona and P.B. Davies

Far infrared rotational transitions of the radical NS have been observed using laser magnetic resonance with an optically pumped spectrometer. The spectra have been recorded at wavelengths of 680 and 514 μm from $\text{C}_2\text{H}_3\text{Br}$ and DCOF , respectively, and have been assigned to individual Zeeman components of the rotational transitions $J = 8.5 \rightarrow 9.5$ and $J = 11.5 \rightarrow 12.5$ in the lowest vibrational level of its ${}^2\Pi_{3/2}$ ground electronic state. The spectra show partly resolved structure due to hyperfine splitting and Λ doubling.

Far infrared LMR spectra of a sulphur radical have been detected with a water vapour discharge laser oscillating on the 108 μm D_2O line. The spectra are tentatively attributed to HCS which has not been detected before and the assignment is based mainly on chemical evidence at this stage. The spectra can be generated from different sources and the most intense is the reaction of F atoms with dimethyl-disulphide. Experiments are now under way to detect much lower J transitions using an optically pumped LMR spectrometer.

P.J. Bruna

For a large number of HAB, ABH radicals containing the atoms C,N,O,Si,P and S MRD-CI calculations are undertaken in order to study their ground state configuration and equilibrium geometry; various calculations for excited states and the positive ions are also carried out [1,2].

As expected from the differences in the dissociation energies of HX systems resulting from the first- and second-row of the periodic Table, the most stable HAB isomer is found to be that in which the hydrogen is bond to the first-row atom. The radical HPO is an exception in this respect.

- [1] Buenker, R.J., Bruna, P.J. and Peyerimhoff, S.D., Israel J. Chem. 19 (1980) 309
- [2] Bruna, P.J., Hirsch, G., Buenker, R.J. and Peyerimhoff, S.D., 1983, Molecular Ions, Geometry and Electronic Structures, NATO, ASI, Series B: Physics, Vol. 90, edited by J. Berkowitz and K.O. Groeneveld (Plenum Publ. Co.), pp. 309

P. JANSSEN

EPR in materials with a high magnetization can be hampered by demagnetizing effects. The correction to be applied to account for this can only be made for a suitable sample shape. Moreover the magnetization and the molecular field constant must be known.

Often these difficulties can be overcome by the use of magnetic fields high enough to saturate the magnetization. The g-value can then be obtained from the slope of the resonance condition if the resonance field is measured as a function of frequency.

Another reason for using high magnetic fields is that in some of these materials the coupling between the spins is almost entirely dipolar. The resulting linewidth is very large and often these measurements can only be done in diluted samples. In high fields the lines can be narrower and the experiment can be done in the undiluted material.

The use of these relatively high fields entails the use of frequencies in the FIR region.

We present here two samples which have also some intrinsic interest. The first is the case of Tm^{3+} ions in TmVO_4 , the other is about Dy^{3+} ions in DAG. Using an optically pumped FIR laser and an HCN laser as radiation sources, we have observed several resonances in the materials. The results can be compared with theories and with data from other types of experiments. In the case of TmVO_4 more resonance lines are seen than we can account for. In DAG, we find a linewidth which is unexpectedly large.

P9 Ab Initio Study of the $X^2\Pi_1$ State of OH: Spin-Orbit Splitting, Λ -Doubling and Einstein Coefficients

R. de Vivie, R. Klotz, C.M. Marian and S.D. Peyerimhoff

The $X^2\Pi_1$ state of OH changes its electronic character from $3\sigma^2 1\pi^3$ to $3\sigma 1\pi^3 \sigma^*$ along the path from equilibrium to $O(^3P) + H(^2S)$ dissociation. This situation leads to a variation of molecular properties with increasing internuclear separation. In the present work the r -dependence has been calculated for dipole moment μ , the spin-orbit parameter A as well as for the Λ -doubling, employing thereby highly correlated wavefunctions. First-order spin-orbit splitting has been studied in the entire range, while second order contributions due to higher electronic states were studied at the equilibrium geometry only.

The $\mu(R)$ dependence was calculated for both the $X^2\Pi_1$ and the first $A^2\Sigma^+$ state. The corresponding vibrational wavefunctions are employed to estimate the Einstein coefficients for IR absorption^{a)}.

a) W. Quade, Diplomarbeit, Bonn 1982

P10 Low-lying Electronic States and Franck-Condon Factors for SiN, SiP, P₂⁺, Si₂⁻, CSi⁻, SiP⁺ and SiN⁺ according to MRD-CI Calculations

V. Krumbach, H. Dohmann, J. Anglada, P.J. Bruna and S.D. Peyerimhoff

The 9-valence electron radicals SiN and CSi⁻ possess X²Σ⁺ (σπ⁴) ground states while the first excited A²Π_i (σ²π³) states are placed in each case in the 1000 cm⁻¹ - 3000 cm⁻¹ energy region.

The isoelectronic second-row systems Si₂⁻, SiP and P₂⁺ are characterized by a stabilization of the ²Π_(u) state in comparison with the ²Σ_(g)⁺ state: in Si₂⁻ the energy difference between both states is practically zero, the P₂⁺ ion possesses a X²Π_u state while the calculations predict a ²Π ground state for SiP. In these species the ²Π_(u) - ²Σ_(g)⁺ separation lies between 0-2100 cm⁻¹ [1].

The theoretical calculations also indicate that in SiP⁺ and SiN⁺ the first electronic transition X³Σ⁻ - A³Π are placed in the infrared region [2].

In all systems discussed the Franck-Condon factors as well as other electronic states will be presented.

[1] Bruna, P.J., Dohmann, H., Anglada, J., Krumbach, V., Peyerimhoff, S.D. Bunker, R.J., J. Mol. Structure (THEOCHEM), 93 (1983) 309

[2] Dohmann, H., Bruna, P.J., Peyerimhoff, S.D. and Bunker, R.J., Mol. Phys. (1984), in press

P11 Ab initio calculation of the CH⁺ ion near its dissociation limits

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We have calculated all the potential curves for the electronic states of CH⁺ correlating with the lowest dissociation limits C⁺(²P) + H(²S). The Hamiltonian employed the spin-orbit interaction, which at the dissociative region asymptotically splits the molecular levels into the corresponding C⁺(²P_{1/2}) and C⁺(²P_{3/2}) atomic limits.

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