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SEQUENTIAL EXCITATION PREPARATION OF MOLECULAR ENERGY  
LEVELS WITH SPECIAL (U) MASSACHUSETTS INST OF TECH  
CAMBRIDGE DEPT OF CHEMISTRY R W FIELD ET AL 06 JAN 86

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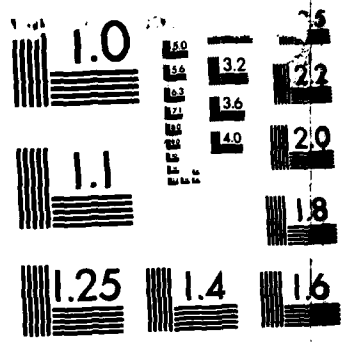
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<p>A. Stimulated Emission Pumping Studies of Formaldehyde — Our SEP studies of H<sub>2</sub>CO are essentially complete. They have yielded an unprecedentedly complete set of anharmonic constants for a 4-atom molecule. SEP studies of D<sub>2</sub>CO have begun but the spectra appear much more complex and congested.</p> <p>B. Quantum Ergodicity in H<sub>2</sub>CO — The non-rotating levels are well organized and unambiguously assignable as normal mode combination and overtone vibrational states. By J=10, K<sub>a</sub>=2 the rotation-vibration levels are intrinsically unassignable, but the spectral density of states is not equal to the total density of states. The spectroscopic distinction between organized and disorganized states is not reflected by any so-far measurable difference in the collisional depopulation rates for organized vs. disorganized levels.</p> <p>C. Collisional Studies in H<sub>2</sub>CO — Several new techniques have been demonstrated on H<sub>2</sub>CO/H<sub>2</sub>CO and H<sub>2</sub>CO/He or Ar rotational energy transfer (RET), Transient Gain Spectroscopy (TGS) and Transient Polarization.</p>			
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MATTHEW J. KEMPER  
Chief, Technical Information Division

18. (continued):

Anticrossing and Quantum Beat Spectroscopy, Barrier to Dissociation, Rotational Energy Transfer, Formaldehyde.

19. (continued):

Spectroscopy (TPS) have been applied to the  $H_2CO \tilde{A} \ ^1A_2$  state. RET Follows dipole propensity rules and the rate of elastic reorientation is found to be negligible relative to the total of inelastic rates. Transient Absorption Polarization Spectroscopy (TAPS) has been applied to highly excited ( $11,400/cm^{-1}$ ) vibrational levels of the  $H_2CO \tilde{X} \ ^1A_1$  state.

## B. Research Objectives

1. Apply the Stimulated Emission Pumping (SEP) technique to highly excited vibrational levels of  $\text{H}_2\text{CO}$  and  $\text{D}_2\text{CO}$ .
2. Discover whether the rotation-vibration levels of  $\text{H}_2\text{CO}/\text{D}_2\text{CO}$  remain well organized at chemically significant levels of vibrational excitation.
3. Develop new multiple resonance spectroscopic techniques capable of measuring rotational energy transfer rates (RET) in highly excited vibrational levels of  $\text{H}_2\text{CO}$ .
4. Develop statistical diagnostics for quantum ergodicity which are applicable to real SEP spectra of  $\text{H}_2\text{CO}/\text{D}_2\text{CO}$ .

## C. Status of Research Effort

Progress toward all of the cited objectives has been made. Research in all four areas is continuing under a new AFOSR grant.

1. Our SEP spectroscopic studies of  $\text{H}_2\text{CO}$  are essentially complete. They have yielded an unprecedentedly complete set of anharmonic constants for a 4-atom molecule. Experiments on  $\text{D}_2\text{CO}$  have begun, but the spectra appear much more complex and congested owing to the higher vibrational density of states and the smaller rotational constants for  $\text{D}_2\text{CO}$  vs.  $\text{H}_2\text{CO}$ .  $\text{D}_2\text{CO}$  SEP experiments are temporarily suspended pending development of a suitable diagnostic for quantum ergodicity.

2. We have found that the vibration-rotation levels of  $\text{H}_2\text{CO}$  are well organized at low-J up to at least  $9300\text{ cm}^{-1}$ , but nearly completely ergodic at higher-J. We are now attempting to discover whether levels which are organized (vibrationally assignable) display any systematic differences in collisional properties from levels which are quantum ergodic (intrinsically unassignable). To date our studies of  $\text{H}_2\text{CO}/\text{H}_2\text{CO}$  collisions have shown no significant difference in total depopulation rate for low-J vs. high-J levels.

We expect that such differences are more likely to be evident in H<sub>2</sub>CO/He or Ar collisions; initial experiments of this type have been successful and are being analyzed.

3. We have demonstrated several techniques for the first time on H<sub>2</sub>CO: Transient Gain Spectroscopy (TGS), Transient Polarization Spectroscopy (TPS), and Transient Absorption Polarization Spectroscopy (TAPS). TGS and TPS were developed and tested on H<sub>2</sub>CO  $\bar{X}^1A_2$  RET. Total depopulation and total depolarization rates were shown to be identical. State-to-state RET rates were measured by both TGS and TPS, again in substantial agreement. Owing to the non-linear nature of TPS, it is much less suitable for measuring state-to-state rates than TGS. TAPS has been used to obtain total depolarization rates for several rotation-vibration levels of H<sub>2</sub>CO  $\bar{X}^1A_1$  at 11,400 cm<sup>-1</sup>. H<sub>2</sub>CO/H<sub>2</sub>CO and H<sub>2</sub>CO/Ar and He collisions have been studied. Preliminary results suggest that TAPS state-to-state RET studies will be possible.

4. Using our complete set of anharmonic Dunham constants and the ab initio cubic force field for H<sub>2</sub>CO as a starting point, we have begun numerical studies of the effect of anharmonic coupling parameters on the spectrum of formaldehyde. We are attempting to identify a statistical diagnostic which will enable us to deduce what fraction of energetically accessible phase space is accessible to a molecule subsequent to various preparations and how long does it take for the molecule to explore uniformly this accessible fraction of phase space. Two statistical diagnostics appear to be promising. Once we know what to look for in our spectra, we will begin to generate SEP spectra of D<sub>2</sub>CO in the 5000-9500 cm<sup>-1</sup> region of vibrational excitation.



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D. Cumulative List of Publications Resulting from AFOSR Supported Research

"The CaO D,d<sup>1,3</sup>Δ-a<sup>3</sup>Π System: Sub-Doppler Spectrum, Rotational Analysis, and Deperturbation". R.F. Marks, R.A. Gottscho, and R.W. Field, *Physica Scripta* 25, 312-328 (1982).

"The Orange Arc Bands of CaO: Analysis of a D,d<sup>1,3</sup>Δ-a<sup>3</sup>Π System", R.F. Marks, H.S. Schweda, R.A. Gottscho, and R.W. Field, *J. Chem. Phys.* 76, 4689-4691 (1982).

"Selective Vibrational Excitation of Formaldehyde  $\bar{X}^1A_1$  by Stimulated Emission Pumping", D.E. Reisner, P.H. Vaccaro, C. Kittrell, R.W. Field, J.L. Kinsey and H.-L. Dai, *J. Chem. Phys.* 77, 573-575 (1982).

"Single Eigenstate Polyatomic Molecule Vibrational Spectroscopy at 1-4eV", H.-L. Dai, E. Abramson, R.W. Field, D. Imre, J.L. Kinsey, C.L. Korpa, D.E. Reisner, and P.H. Vaccaro, *Springer Series Opt. Sci.* 40, 74-77 (1983).

"Electric Dipole Moments of Excited Vibrational Levels in the  $\bar{X}^1A_1$  State of Formaldehyde by Stimulated Emission Spectroscopy", P.H. Vaccaro, J.L. Kinsey, R.W. Field, and H.-L. Dai, *J. Chem. Phys.* 78, 3659-3664 (1983).

"Long Range Behavior of the Gerade States Close to the  $^2P_{3/2} + ^2P_{3/2}$  Iodine Dissociation Limit by Laser-Induced Fluorescence Fourier-Transform Spectroscopy", F. Martin, S. Churassy, R. Bacis, R.W. Field, and J. Vergès, *J. Chem. Phys.* 79, 3725-3737 (1983).

"Direct Observation of High-Lying  $^3\Pi_g$  States of the Na<sub>2</sub> Molecule by Optical-Optical Double Resonance," Li Li and R.W. Field, *J. Phys. Chem.* 87, 3020-3022 (1983).

"Stimulated Emission Spectroscopy: A Complete Set of Vibrational Constants for  $\bar{X}^1A_1$  Formaldehyde", D.E. Reisner, R.W. Field, J.L. Kinsey, and H.-L. Dai, *J. Chem. Phys.* 80, 5968-5978 (1984).

"Laser Population of Highly Excited Vibrational Levels of Molecules", E. Abramson, H.-L. Dai, R.W. Field, D.G. Imre, J.L. Kinsey, C. Kittrell, D.E. Reisner, and P.H. Vaccaro, pp. 393-404 in *Lasers as Reactants and Probes in Chemistry*, (eds. W.M. Jackson and A.B. Harvey) Howard University Press, 1985.

"Rotation Induced Vibrational Mixing in  $\bar{X}^1A_1$  Formaldehyde: Nonnegligible Dynamical Consequences of Rotation", H.-L. Dai, C.L. Korpa, J.L. Kinsey, and R.W. Field, *J. Chem. Phys.* 82, 1688-1701 (1985).

State-Specific Rates of H<sub>2</sub>CO(S<sub>0</sub>) → H<sub>2</sub> + CO at Energies Near the Top of the Barrier: A Violation of RRKM Theory?", H.-L. Dai, R.W. Field, and J.L. Kinsey, *J. Chem. Phys.* 82, 1606-1607 (1985).

Publications (continued):

"Intramolecular Vibrational Dynamics Including Rotational Degrees of Freedom: Chaos and Quantum Spectra", H.-L. Dai, R.W. Field, and J.L. Kinsey, J. Chem. Phys. 82, 2161-2163 (1985).

"Rotational Relaxation in the  $\text{H}_2\text{CO } \tilde{A} \ ^1\text{A}_2$  State by Transient Gain Spectroscopy", P.H. Vaccaro, R. Redington, J. Schmidt, J.L. Kinsey, and R.W. Field, J. Chem. Phys. 82, 5755-5756 (1985).

"The Electronic Assignments of the Violet Bands of Sodium", G. Pichler, J.T. Bahns, K.M. Sando, W.C. Stwalley, D.D. Konowalow, Li Li, R.W. Field, and W. Mueller, Chem. Phys. Lett. 00, 000-000 (1986).



## E. Personnel

### 1. Visiting Scientists

Prof. Richard Redington ( $\text{H}_2\text{CO}$  TGS and TPS)  
Texas Tech University  
Lubbock, Texas

### 2. Postdoctoral Associates

Dr. Hai-Lung Dai ( $\text{H}_2\text{CO}$  SEP)  
Dr. Charles Hamilton ( $\text{H}_2\text{CO}$  TPS, TAPS)  
Dr. Jean-Paul Pique (Quantum Ergodicity)  
Dr. Friedrich Temps ( $\text{H}_2\text{CO}$  TSP, TAPS)

### 3. Graduate Students

Scott Halle ( $\text{D}_2\text{CO}$  SEP, Quantum Ergodicity)  
Patrick Vaccaro ( $\text{H}_2\text{CO}$  TGS, TPS, TAPS)

### 4. Undergraduate Students

Ann Zabludoff ( $\text{H}_2\text{CO}$ ,  $\text{D}_2\text{CO}$  Stark Quantum Beats)

F. Interactions: Spoken Papers

1. R.W. Field, "Stimulated Emission Pumping," 181st Meeting of American Chemical Society, Atlanta (Nobel Laureate Signature Award Session), Talk 61.
2. J.L. Kinsey, "Laser Photons as Analytic and Synthetic Reagents in Studies of Reaction Dynamics," 181st Meeting of American Chemical Society, Atlanta (Peter Debye Award Symposium), Talk 19.
3. J.L. Kinsey, "Laser Population of Highly Excited Vibrational Levels of Molecules," Conference on Lasers as Reactants and Probes in Chemistry, Howard University (May 1982).
4. J.L. Kinsey, "An Outsider's View of the Spectroscopy of Polyatomic Systems - Bound and Continuum States," Distinguished Speakers Series, Department of Chemistry, University of Utah (May 1982).
5. J.L. Kinsey, "Stimulated Emission Pumping: An Easy Route to Highly Excited Levels of Polyatomic Molecules," Aerodyne Corp. (January 1982).
6. J.L. Kinsey, same as #5, Brown University, Department of Chemistry (January 1982).
7. J.L. Kinsey, "Study of Vibrationally Hot Molecules by Stimulated Emission," Yale University, Department of Chemistry (February 1982).
8. R.W. Field, "Vibrationally Very Hot Molecules," Laboratoire de Photophysique Moléculaire, Orsay, France (December 1981).
9. R.W. Field, "Do Highly Excited Molecules Have a Structure?" Symposium on Lasers in Spectroscopy and Technology, M.I.T. (May 1982).
10. R.W. Field, "Vibrationally Excited Formaldehyde and Acetylene," Informal Conference on Photochemistry, SRI International (June 1982).
11. R.W. Field, "Stimulated Emission Pumping," Freie Universität Berlin (March 1982).
12. R.W. Field, same as #11, Aerodyne (June 1982).
13. R.W. Field, "Stimulated Emission Pumping: Vibrational Energy Redistribution in  $H_2CO$  and  $HCCH$ ?" Harvard University, Department of Chemistry (February 1983).
14. R.W. Field, same as #13, Notre Dame Radiation Laboratory (March 1983).
15. R.W. Field, same as #13, University of Colorado, Joint Institute of Laboratory Astrophysics (May 1983).
16. R.W. Field, same as #13, Denver University, Department of Chemistry (May 1983).

Interactions: Spoken Papers (continued):

17. R.W. Field, "Vibrationally Hot Molecules: A Search for a Needle in a Haystack," University of Pittsburgh, Department of Chemistry (November 1982).
18. R.W. Field, "Stimulated Emission Pumping," Lasers 82, New Orleans (December 1982).
19. R.W. Field, same as #18, North East Regional Meeting of the American Chemical Society, Hartford (June 1983).
20. H.-L. Dai, P.H. Vaccaro, E. Abramson, M. Lombardi, K.K. Innes, R.W. Field, and J.L. Kinsey, "Vibrational Energy Redistribution in  $\text{H}_2\text{CO}$  and  $\text{HCCH}$ ? Quantum Beat and Stimulated Emission Spectroscopy," XIth International Conference on Photochemistry, University of Maryland (August 1983).
21. R.W. Field, "Stimulated Emission and Quantum Beat Spectroscopy: The  $\text{H}_2\text{CO} \rightarrow \text{H}_2 + \text{CO}$  Barrier and Quantum Chaos in the Acetylene  $\tilde{X}^1\Sigma_g^+$  State," International Workshop on Primary Photophysical Processes, Heßrsching, Germany (October 1983).
22. R.W. Field, "A Time Independent View of Intramolecular Vibrational Redistribution: Coriolis Perturbations in Formaldehyde and Quantum Chaos in Acetylene," International Conference on Radiationless Transitions, Newport Beach, California (January 1984).
23. J.L. Kinsey, "Stimulated Emission and Quantum Beat Spectroscopy," American Physical Society, Los Angeles (March 1983).
24. R.W. Field, same as #22, University of Arizona, Department of Chemistry (November 1983).
25. R.W. Field, same as #22, Northeastern University, Department of Chemistry (November 1983).
26. R.W. Field, same as #22, Syracuse University, Department of Chemistry (February 1984).
27. R.W. Field, "Stimulated Emission Spectroscopy: Structure, Isomerization, and Chaos", University of Pennsylvania, Department of Chemistry (April 1984).
28. R.W. Field, same as #27, MIT Modern Optics and Spectroscopy Series (May 1984).
29. J.L. Kinsey, "Evidence for Quantum Chaos in the Stimulated Emission Pumping Spectrum of Acetylene near  $28000 \text{ cm}^{-1}$ ", Conference on Quantum Chaos, Los Alamos National Lab. (March 1983).

Interactions: Spoken Papers (continued):

30. J.L. Kinsey, "Energy Redistribution in Acetylene?", DOE Contractors' Meeting, Brookhaven National Lab. (May 1983).
31. J.L. Kinsey, "Chemical Dynamics Studied by Emission Spectroscopy of Dissociating Molecules", University of North Carolina (September 1983).
32. J.L. Kinsey, same as #31, University of California (November 1983).
33. J.L. Kinsey, same as #31, Tulane University (November 1983).
34. J.L. Kinsey, same as #31, Texas A&M University (December 1983).
35. J.L. Kinsey, same as #31, Rice University (December 1983).
36. J.L. Kinsey, same as #31, Harvard University (January 1984).
37. J.L. Kinsey, same as #31, Northeastern University (January 1984).
38. J.L. Kinsey, same as #31, University of Rochester (February 1984).
39. J.L. Kinsey, "Stimulated Emission and Quantum Beat Spectroscopy of Formaldehyde and Acetylene", 8th International Symposium on Gas Kinetics, University of Nottingham, England (July 1984).
40. P.H. Vaccaro, "Rotational Relaxation in the  $v_4=1$  Vibrational Level of  $H_2CO$  A  $A_2$  By Transient Gain Spectroscopy", Molecular Spectroscopy Symposium at Ohio State University (June, 1984).
41. A. Zabludoff, "Dipole Moments in the Out-of-Plane Bending Levels of A  $A_2$  Formaldehyde- $h_2$  and  $-d_2$ ", Molecular Spectroscopy Symposium at Ohio State University (June, 1984).
42. R.W. Field, "A Spectroscopic Quest for the Holy Grail", University of Texas (January, 1985).
43. R.W. Field, "Structure, Isomerization, and Quantum Ergodicity in  $S_0$  Acetylene", Rice University (January, 1985).
44. R.W. Field, "What Does High Resolution Spectroscopy Have to Say About Structure, Chaos, and State-Specific Chemistry?", Shell Research and Development, Houston (January, 1985).
45. R.W. Field, same as #43, Herzberg Institute for Astrophysics, Ottawa (April, 1985).
46. R.W. Field, same as #44, AT&T Laboratories, Murray Hill (April, 1985).
47. R.W. Field, same as #43, Universite Claude Bernard, Lyon, France (June, 1985).

Interactions: Spoken Papers (continued):

48. R.W. Field, same as #44, Universite Paris-Sud, Laboratoire Photophysique Moleculaire (June, 1985).
49. R.W. Field, same as #44, Gordon Conference on Molecular Energy Transfer (July, 1985).
50. R.W. Field, "Spectroscopic Studies of Tunnelling in Li<sub>2</sub>, Na<sub>2</sub>, and Acetylene", Tunneling Symposium, American Chemical Society National Meeting, Chicago (September, 1985).
51. R.W. Field, "Quantum Ergodicity: Real Spectra of a Real Molecule", Workshop on Quantum Chaos, University of Rochester (October, 1985).
52. R.W. Field, same as #44, Columbia University (October, 1985).
53. R.W. Field, same as #44, Wayne State University (October, 1985).

G. Patents

None.

## COMPLETED PROJECT SUMMARY

1. TITLE: Sequential Excitation Preparation of Molecular Energy Levels with Special Structural and Chemical Properties
2. PRINCIPAL INVESTIGATORS: Dr. Robert W. Field  
and  
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3. INCLUSIVE DATES: 01 October 1984 - 30 September 1985
4. CONTRACT/GRANT NUMBER: AFOSR F49620-85-C-0006
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6. SENIOR RESEARCH PERSONNEL: Dr. H.-L. Dai  
Dr. F. Temps  
Dr. C. Hamilton  
Dr. R. Redington
7. JUNIOR RESEARCH PERSONNEL: S. Halle  
P.H. Vaccaro  
A. Zabludoff
8. PUBLICATIONS:

"Stimulated Emission Spectroscopy: A Complete Set of Vibrational Constants for  $\bar{X} \ ^1A_1$  Formaldehyde", D.E. Reisner, R.W. Field, J.L. Kinsey, and H.-L. Dai, J. Chem. Phys. 5968-5978 (1984).

"Rotation Induced Vibrational Mixing in  $\bar{X} \ ^1A_1$  Formaldehyde: Nonnegligible Dynamical Consequences of Rotation", H.-L. Dai, C.L. Korpa, J.L. Kinsey, and R.W. Field, J. Chem. Phys. 82, 1688-1701 (1985).

"State-Specific Rates of  $H_2CO(S_0) \rightarrow H_2 + CO$  at Energies Near the Top of the Barrier: A Violation of RRKM Theory?", J. Chem. Phys. 82, 1606-1607 (1985).

"Intramolecular Vibrational Dynamics Including Rotational Degrees of Freedom: Chaos and Quantum Spectra", H.-L. Dai, R.W. Field, and J.L. Kinsey, J. Chem. Phys. 82, 2161-2163 (1985).

"Rotational Relaxation in the  $H_2CO \ \bar{A} \ ^1A_2$  State by Transient Gain Spectroscopy", P.H. Vaccaro, R. Redington, J. Schmidt, J.L. Kinsey, and R.W. Field, J. Chem. Phys. 82, 5755-5756 (1985).

"Laser Population of Highly Excited Vibrational Levels of Molecules", E. Abramson, H.-L. Dai, R.W. Field, D. Imre, J.L. Kinsey, C. Kittrell, D.E. Reisner, and P.H. Vaccaro, pp. 393-404 in Lasers as Reactants and Probes in Chemistry (eds. W.M. Jackson and A.B. Harvey), Howard University Press, 1985.

"The Electronic Assignments of the Violet Bands of Sodium", G. Pichler, J.T. Bahns, K.M. Sando, W.C. Stwalley, D.D. Konowalow, Li Li, R.W. Field, and W. Mueller", Chem. Phys. Lett. 00, 000-000 (1986).

## 9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

### A. Stimulated Emission Pumping Studies of Formaldehyde

We have learned a great deal from SEP spectra (Stimulated Emission Pumping) about the predominant normal mode character of many H<sub>2</sub>CO and D<sub>2</sub>CO vibrational levels in the 5000-12000 cm<sup>-1</sup> excitation region on the  $\bar{X}^1A_1$  ground electronic state surface. Spectroscopy has shown that:

1. Nonrotating levels exhibit "assignable" vibrational spectra up to the highest E observable so far. "Assignable" means that the energy levels are well represented by Dunham type expressions:

$$E_v = \sum_{i=1}^6 [\omega_i (v_i + 1/2)] - \sum_{j=1}^6 \omega x_{ij} (v_i + 1/2)(v_j + 1/2)$$

and the only levels that appear in our spectra are those calculated to have large Franck-Condon overlap with the  $\bar{A}^4l$  levels from which our SEP spectra are recorded.

2. At  $J > 5$ ,  $K_a > 1$ ,  $J \neq K_a$  most of the vibrational regularity in the spectrum disappears. The spectra become complicated and unassignable. We believe this reflects the almost complete loss of localization of the eigenstates onto any conceivable separable Hamiltonian basis set.

3. A marked departure from the behavior in item #2 above is found for the high overtones of the carbonyl stretch. The  $2_n$  levels for  $n=4,5,7$  appear to be free of the state-mixing effects found for all other levels.

Our present experiments are designed to discover whether spectroscopic information about level "assignability" or localization has any relevance to collisional or chemical processes. Does the molecule remember that it is in a special, localized eigenstate or is the collision so violent that the molecule forgets the nature of its initial state. This is a very important question in light of the fact that spectroscopy identifies localized levels embedded in a dense manifold of non-localized or ergodic states. Ideally, we would want to look for level specific chemistry, but such a study would be vastly more difficult than the measurements of rotationally inelastic rates which we have recently been able to perform.

### B. Collisional Studies of H<sub>2</sub>CO $\bar{X}^1A_2$

Although our goal is to look at state-to-state rotational energy transfer (RET) at high excitation energy in the  $\bar{X}$ -state, we started by developing and testing techniques for monitoring RET in the  $\bar{A}$ -state.

1. Transient Gain Spectroscopy (TGS). A cw laser probes for gain produced by pulsed population of a specific rotational level ( $J_{Ka,Kc} = 13_2,1_2$ ) of the  $\tilde{A} 4^1$  level. The observed total depopulation rate for the initially populated rotational level is, for  $H_2CO/H_2CO$  collisions, found to be

$$k_{TOTAL}(\tilde{A} 4^1 13_2,1_2) = 110.5 \pm 3.1 \mu\text{sec}^{-1}\text{Torr}^{-1} .$$

This rate is exactly what is expected for a dipole-dipole relaxation process because it is in excellent agreement with the corresponding rate for the  $\tilde{X} 0_0$  levels measured by microwave pressure broadening

$$k_{TOTAL}(\tilde{X} 0_0, J_{Ka,Kc}) = 150 \mu\text{sec}^{-1}\text{Torr}^{-1}$$

because

$$k_{TOTAL}(\tilde{A}) = \frac{\mu_{\tilde{A}}}{\mu_{\tilde{X}}} k_{TOTAL}(\tilde{X})$$

where  $\mu$  is the electric dipole moment. Incidentally, we have made the most accurate measurements of  $\mu_{\tilde{A}}$  and extended knowledge of  $\mu_{\tilde{X}}$  to much higher vibrational levels than had been studied previously.

2. Transient Polarization Spectroscopy (TPS). A cw laser probes for polarization transferred from the initially prepared  $J_{Ka,Kc}$  level to another nearby level. This scheme was deemed necessary because amplitude noise on the cw dye laser in the 1-100 MHz region would make transient absorption spectroscopy in the  $\tilde{X}$ -state prohibitively difficult. By TPS we found that the total depopulation rate of  $\tilde{A} 4^1 13_2,1_2$  measured by TGS was identical, to within 5%, to the corresponding depolarization rate measured by TPS. This means that elastic reorientation of  $J=13$  proceeds at a rate at least 20 times slower than the total rotationally inelastic rate.

3. State-to-State RET measured by TGS and TPS. We were able to measure state-to-state rates in  $\tilde{A} 4^1$  by the TGS scheme, and recently also by the TPS scheme. The observed rates are

$$k(13_2,1_2 \rightarrow 14_2,1_3) = 40 \pm 6 \mu\text{sec}^{-1}\text{Torr}^{-1}$$

$$k(13_2,1_2 \rightarrow 12_2,1_1) = 31 \pm 8 \mu\text{sec}^{-1}\text{Torr}^{-1} .$$

This is probably the first measurement of state-to-state RET in an excited state of a polyatomic molecule. A remarkable result is that

$$\frac{k(13_2,1_2 \rightarrow 14_2,1_3) + k(13_2,1_2 \rightarrow 12_2,1_1)}{k_{TOTAL}(\tilde{A} 4^1 13_2,1_2)} = 0.64 \pm 0.10 .$$



The two predicted strongest a-dipole ( $J_{Ka} + J_{\pm 1, Ka}$ ) rates account for 64% of the total depopulation rate! This means that RET in  $H_2CO \bar{A}^1$  follows dipole propensity rules astonishingly well.

C. Collisional Studies of  $H_2CO \bar{A}^1$  at  $E_{vibration} \approx 11,400 \text{ cm}^{-1}$

Pulsed SEP is used to prepare a transient population in the  $\bar{X} 2444 5_{1,4}$  level at  $\sim 11,400 \text{ cm}^{-1}$ . A cw probe laser monitors the decay of the prepared polarization (the rate measured by TPS and TAPS is actually twice the actual molecular depolarization rate). We have measured depolarization rates for the  $4_{1,3}, 5_{1,4}, 6_{1,5}$  and  $13_{2,12}$  levels and found that they are in good agreement with each other,

$$k_{TOTAL}(\bar{X} 2444 J_{Ka} K_c) = 115 \pm 3 \text{ } \mu\text{sec}^{-1} \text{ Torr}^{-1},$$

which is only 77% as large as  $k_{TOTAL}(\bar{X} 0_0, J_{Ka}, K_c)$ . This decrease is qualitatively but not quantitatively compatible with the expected smaller dipole moment for the  $\bar{X} 2444$  level than  $\bar{X} 0_0$

$$\mu(0_0) = 2.331 \text{ Debye}$$

$$\mu(2444) = 2.318 \text{ Debye.}$$

What is remarkable is that, even though the density of final states for this inelastic process has increased by  $10^3$  from  $\sim 10^{-3}$  per  $\text{cm}^{-1}$  at  $E=0$   $\text{cm}^{-1}$  to  $\sim 1$  per  $\text{cm}^{-1}$  at  $E=11,400 \text{ cm}^{-1}$ , the total depopulation rate decreases!

Our initial attempt to monitor state-to-state processes at high levels of vibrational excitation by Transient Absorption Polarization Spectroscopy (TAPS) appears to have been successful.

To summarize: all three schemes described here (TGS, TPS, TAPS) have been successfully applied to polyatomic molecules for the first time. They demonstrate the power of SEP schemes to populate selectively highly excited rotation-vibration levels. These experiments will provide a fundamental assessment of the relationship between spectroscopic observations of isolated molecule properties and state-to-state variations of these properties manifest in collisional processes.

AFOSR Program Manager: Dr. F.J. Wodarczyk

**REPORT OF INVENTIONS AND SUBCONTRACTS**

(Pursuant to "Patent Rights" Contract Clause) (See Instructions on Reverse Side.)

1a. NAME OF CONTRACTOR/SUBCONTRACTOR R. F. Id/J. Kinsey	2a. NAME OF GOVERNMENT PRIME CONTRACTOR	3. TYPE OF REPORT (check one) <input type="checkbox"/> INTERIM <input checked="" type="checkbox"/> FINAL	
1b. ADDRESS (include Zip Code) Dept. of Chem., M.I.T. Cambridge, MA 02139	2b. ADDRESS (include Zip Code) 84--10-01	4. REPORTING PERIOD (YYMMJJ) FROM 84-10-01 TO 85-09-30	
c. CONTRACT NUMBER F49620-85-C-0006		CONTRACT NUMBER	
d. AWARD DATE (YYMMJJ)		AWARD DATE (YYMMJJ)	

**SECTION I - SUBJECT INVENTIONS**

a. NAME OF INVENTOR(S) (Last, First, M.I.)	b. TITLE OF INVENTION(S)	c. DISCLOSURE NO., PATENT APPLICATION SERIAL NO. OR PATENT NO.	d. ELECTION TO FILE PATENT APPLICATIONS				e. CONFIRMATORY INSTRUMENT OR ASSIGNMENT FORWARDED TO CONTRACTING OFFICER	
			UNITED STATES	FOREIGN	YES	NO		
NONE			YES	NO	YES	NO	YES	NO

7. EMPLOYER OF INVENTOR(S) NOT EMPLOYED BY CONTRACTOR/SUBCONTRACTOR.	8. ELECTED FOREIGN COUNTRIES IN WHICH A PATENT APPLICATION WILL BE FILED.
9. NAME OF INVENTOR (Last, First, M.I.)	10. FOREIGN COUNTRIES OF PATENT APPLICATION
11. NAME OF EMPLOYER	TITLE OF INVENTION
12. ADDRESS OF EMPLOYER (include Zip Code)	

**SECTION II - SUBCONTRACTS (Containing a "Patent Rights" clause)**

a. NAME OF SUBCONTRACTOR(S)	b. ADDRESS (include Zip Code)	c. SUBCONTRACT NO.(S)	d. "PATENT RIGHTS" CLAUSE NO.		e. DESCRIPTION OF WORK TO BE PERFORMED UNDER SUBCONTRACT(S)	f. SUBCONTRACT DATES (YYMMJJ)	
			DATE (YYMM)	AWARD		ESTIMATED COMPLETION	

**SECTION III - CERTIFICATION**

7. CERTIFICATION OF REPORT BY CONTRACTOR/SUBCONTRACTOR (Not required if  Small Business or  Non-Profit organization) (Check appropriate box)

8. NAME OF AUTHORIZED CONTRACTOR/SUBCONTRACTOR OFFICIAL  
(Last, First, M.I.) **Field, Robert W.**

9. TITLE **Professor of Chemistry**

Signature of Authorized Contractor/Subcontractor Official: **Robert W. Field**

DATE (YYMMJJ) **86-01-06**

END

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