Technical Progress Report

DOE/ER/13671--4

on

DE91 005981

DEPARTMENT OF ENERGY Grant DE-FG02-87ER13671

Period: February 1, 1990 - August 31, 1990

Document No. DOE/ER/13671-4

Spectroscopic and Dynamical Studies of Highly Energized Small Polyatomic Molecules

Robert W. Field

Co-principal Investigator

Robert J. Silbey

Co-principal Investigator

Department of Chemistry
Massachusetts Institute of Technology
77 Massachusetts Avenue
Cambridge, Massachusetts 02139

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

MASTER

1. The HCO $\tilde{B}^2A'$ - $\tilde{X}^2A'$ System

The formyl radical, in addition to its importance as a combustion intermediate, is emerging as a watershed molecule in Physical Chemistry. Many experiments and theoretical calculations sample global and detailed features of the lowest energy potential surface of HCO in complementary ways.

We have shown that Richard Dixon's analysis of the hydrocarbon flame bands is essentially correct. The $\tilde{B}$ and $\tilde{C}$ states turn out to be a single $^2A'$ state, which at least in its low vibrational and low-J,K levels is sufficiently free of predissociation to provide a basis for sensitive LIF monitoring of HCO via the extremely strong, hybrid a, b-polarized $\tilde{B}$ - $\tilde{X}$ system. The $\tilde{B}$ - $\tilde{X}$ system has a much higher oscillator strength and fluorescence quantum yield than the $\tilde{A}$ - $\tilde{X}$ system. We have completed a detailed rotational analysis and fit of the $\tilde{B}$ - $\tilde{X}$ O_0^0 band. A comparison of early- and late-gated fluorescence excitation spectra of the $\tilde{B}$ - $\tilde{X}$ O_0^0 band shows that some high-J,K levels have significantly shorter lifetimes than the low-J,K levels. We plan systematic study of the rotational and vibrational mechanisms of predissociation and collisional quenching in the HCO $\tilde{B}$ -state. The quenching study will show whether the $\tilde{B}$ - $\tilde{X}$ system really is superior to the $\tilde{A}$ - $\tilde{X}$ system at the > 100 Torr pressures typically relevant for *in situ* combustion diagnostics.

We have recorded SEP spectra of HCO. These spectra sample vibrational "levels" or "resonances" in the $\tilde{X}^2A'$ state at energies well above (~ 4000 cm^{-1}) the H—CO dissociation limit. Our initial results show that the $(\nu_{CH}, \nu_{CO}, \nu_{bend}) = (0, 5, 0)$ level has a longer lifetime ($\Gamma = 0.8$ cm^{-1}) than the lower lying $(0, 4, 1)$ level ($\Gamma = 6$ cm^{-1}). This mode specificity demonstrates the correctness of *ab initio* predictions of long-lived resonances and the relative effectiveness of C—H vs. C—O vs. bend vibrations in promoting dissociation. We plan to extend our SEP studies to other vibrational levels of the $\tilde{X}^2A'$ state, especially those predicted to lie close to the dissociation threshold, and to document the vibrational and rotational dependence of unimolecular dissociation rates.

In order to record SEP spectra of the HCO radical, we had to modify our SEP detection scheme to permit photolytic generation of HCO (from acetaldehyde) and to suppress spurious signals due to excitation of non-HCO species (i.e., acetaldehyde, CH_3 , H_2CO , etc.) by the DUMP laser. Our photolysis SEP setup should now make it possible for us to record SEP spectra of other photolytically generated species.

2. Optical-Optical Double Resonance (OODR) Studies of Acetylene.

We have recorded onto diskettes an enormous quantity of SEP spectra of acetylene. In the process of assembling all of these spectra into large and systematic data files, we discovered many unusual features which did not belong to $\tilde{A}^1A_u-\tilde{X}^1\Sigma_g^+$ SEP spectra of acetylene. Among these are two new predissociated singlet valence states. The $\tilde{C}'^1A_g$ state ($T_0 = 62,300 \text{ cm}^{-1}$) is planar, strongly *trans*-bent ($\theta_{\text{CCH}} = 102^\circ$), and formally C—C single-bonded ($\pi^2 \pi^{*2}$). The $\tilde{E}^1B$ state ($T_0 = 74,613 \text{ cm}^{-1}$) is a *non-planar near-trans*, C=C doubly bonded ($\pi^3 \pi^*$) state initially identified by Wilkinson but disputed by virtually all later experimental and theoretical studies. Both of these predissociated states have fully resolvable rotational structure only in OODR spectra of their zero-point vibrational level. Studies of HCCH and DCCD have enabled us to determine the Γ_0 structures in the $\tilde{C}'$ and $\tilde{E}$ states. It appears that, owing to the presence of two H's and two C's, group theory (plus OODR spectroscopy) is capable of distinguishing between a wide array of isomeric forms: planar *trans*, planar *cis*, planar vinylidene, nonplanar near-*trans*, nonplanar near-*cis*, and unequal C-H bond lengths.

We also have observed some strong downward transitions, from the DCCD $\tilde{A}^1A_u v_3=5$ level, into vibrational levels near $28,000 \text{ cm}^{-1}$. There are many features of these spectra which lead us to believe that these new vibrational levels belong to the *cis*-acetylene isomer minimum of the lowest triplet surface. SEP transitions from S_1 (*trans*) to T_1 (*cis*) are made allowed by spin-orbit perturbations between S_1 (*trans*) and T_2 near the *cis-trans* (linear) isomerization barrier. This isomerization barrier on T_2 is not idle speculation; our Zeeman and Stark anticrossing and quantum beat spectra of HCCH have located this T_2 *cis-trans* barrier maximum at an energy near HCCH $S_1 v_3=2$ or 3. We plan systematic study of the *cis*-bent acetylene and vinylidene isomers on the T_1 and T_2 surfaces by "perturbation facilitated" SEP spectroscopy.

3. Zeeman and Stark Anticrossing (ZAC and SAC) and Quantum Beat (ZQB and SQB) Studies of Acetylene

The $J=K=I=0$ levels of HCCH $\tilde{A}^1A_u v_3 = 0-3$ can be populated via hot band transitions (out of $\tilde{X}^1\Sigma_g^+ v_4=1, \ell=1, J=1$). These are the simplest possible levels for monitoring the properties of dark triplet states via ZAC spectroscopy. The density of anticrossings observed as the magnetic field is scanned from 0 to 8 Tesla should be simply related to the density of triplet vibrational levels. The observed rapid increase in ZAC density from $v_3=0$ to $v_3=3$ forces us to conclude that an unprecedented triplet-facilitated $S_1 \rightarrow S_0$ anticrossing mechanism is operative. The reason for the abrupt increase in ZAC density is that the top of the planar *cis-trans*

isomerization barrier on the T_1 or T_2 surface must be located at an energy near $\tilde{A}^1A_u v_3 = 2$ or 3. ZQB, SAC, and SQB experiments confirm this interpretation.

These experiments provide an unusually detailed view of both Intersystem Crossing and Internal Conversion in a small polyatomic molecule. They also provide us with numerous points of spectroscopic access to the acetylene and vinylidene triplet manifolds.

4. The Dissociation Energy of Acetylene, $D_0(\text{HCC—H})$.

When an electric field of 113 kV/cm is applied to acetylene in the $\tilde{A}^1A_u v_3 = 2$ state, several rotational levels exhibit increases in fluorescence decay rates. Such increases in decay rates are normally conclusive evidence for predissociation. After carefully examining what seemed to us to be all conceivable alternative explanations of this electric field induced lifetime shortening effect, we were led to propose an extremely controversial low value of an upper bound on $D_0(\text{HCC—H}) \leq 126.647 \pm 0.002$ kcal/mol. The enormous weight of diverse and elegant experiments and calculations in support of a value for $D_0(\text{HCC—H}) \sim 6$ kcal/mol higher than our value has forced us to reexamine our predissociation interpretation of the electric field induced lifetime shortening effect. The key to our graceful retreat from our probably too-low upper bound is the above-mentioned *cis-trans* barrier triplet-facilitated $S_1 \rightarrow S_0$ interaction.

Publications since 1985 resulting from DOE sponsorship

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

E. Abramson, R.W. Field, D. Imre, K.K. Innes, and J.L. Kinsey, "Fluorescence and Stimulated Emission $S_1 \rightarrow S_0$ Spectra of Acetylene: Regular and Ergodic Regions," J. Chem. Phys. 83, 453-465 (1985).

R. L. Sundberg, E. Abramson, J.L. Kinsey, and R.W. Field, "Evidence of Quantum Ergodicity in Stimulated Emission Pumping Spectra of Acetylene", J. Chem. Phys. 83, 466-475 (1985).

G.J. Scherer, Y. Chen, R.L. Redington, J.L. Kinsey, and R.W. Field, "An Unsuspected Fermi Perturbation in the Acetylene $\tilde{A}^1A_u 3v_3$ Level", J. Chem. Phys. 85, 6315-6323 (1986).

C.E. Hamilton, J.L. Kinsey, and R.W. Field, "Stimulated Emission Pumping: New Methods in Spectroscopy and Molecular Dynamics," Ann. Rev. Phys. Chem. 37, 493-524 (1986).

J.P. Pique, Y. Chen, R.W. Field and J.L. Kinsey, "Chaos and Dynamics on 30fs-1ns Time Scales in Vibrationally Excited Acetylene: Fourier Transform of Stimulated Emission Pumping Spectrum", Phys. Rev. Letts. 58, 475-478 (1987).

R.W. Field, "High Resolution Spectroscopy of Small Molecules", Conference Laser M2P, 1987, J. de Physique C7, 17-28 (1987).

Y. Chen, D.M. Jonas, C.E. Hamilton, P.G. Green, J.L. Kinsey, and R.W. Field, "Acetylene: Isomerization and Dissociation," Berichte der Bunsengesellschaft für Physikalische Chemie, 92 329-336 (1988).

J.-P. Pique, Y. Chen, R.W. Field, and J.L. Kinsey, "Laser Spectroscopy and Quantum Chaos: An Example Through the Fourier Transform of a Stimulated Emission Pumping Spectrum of C_2H_2 at Very High Vibrational Energy", Conference Laser M2P, 1987, J. de Physique C7, 655-657 (1987).

J.P. Pique, Y. Chen, R.W. Field, J.L. Kinsey, and M. Lombardi, "New Order Out of the Chaotic Bath of Highly Excited Vibrational States of C_2H_2 ", Berichte der Bunsengesellschaft für Physikalische Chemie 92, 422-424 (1988).

J.P. Pique, Y.M. Engel, R.D. Levine, Y. Chen, R.W. Field, and J.L. Kinsey, "Broad Spectral Features in the Stimulated Emission Pumping Spectrum of Acetylene", J. Chem. Phys. 88, 5972-5974 (1988).

M.H. Alexander, P. Andresen, R. Bacis, R. Bersohn, F.J. Comes, P.J. Dagdigian, R.N. Dixon, R.W. Field, G.W. Flynn, K.-H. Gericke, B.J. Howard, J.P. Huber, D.S. King, J.L. Kinsey, K. Kleinermanns, A.C. Luntz, A.J. MacCaffery, B. Pouilly, H. Reisler, S. Rosenwaks, E. Rothe, M. Shapiro, J.P. Simons, R. Vasudev, J.R. Wiesenfeld, C. Wittig, and R.N. Zare, "A Nomenclature for Λ Doublet Levels in Rotating Linear Molecules", J. Chem. Phys. 89, 1749-1753 (1988).

R.W. Field, "Pathologically Complex Spectra of Small Molecules: High Resolution Techniques for Displaying Vibrational Chaos and Electronic Simplicity", Conference on Quantum

Electronics and Laser Science, 1989 Technical Digest Series, Vol. 12 (Optical Society of America, Washington, DC), pp. 160-162 (Talk THH2), 1989.

R.W. Field, "Statistical Spectroscopy: Insight or Nonsense?", ILS-IV, 1988, Am. Instit. of Phys. Conf. Proc. 191, 673-682 (1988).

P.G. Green, J.L. Kinsey, and R.W. Field, "A New Determination of the Dissociation Energy of Acetylene", J. Chem. Phys. 91, 5160-5163 (1989).

Y. Chen, D.M. Jonas, J.L. Kinsey, and R.W. Field, "High Resolution Spectroscopic Detection of Acetylene $\leftrightarrow$ Vinylidene Isomerization by Spectral Cross-Correlation" J. Chem. Phys. 91, 3976-3987 (1989).

J. Vander Auwera, T.R. Huet, M. Herman, C. Hamilton, J.L. Kinsey, and R.W. Field, "The $\tilde{A}^1A_u$ Electronic State of Monodeuterated Acetylene", J. Mol. Spectrosc. 137, 381-395 (1989).

C.E. Hamilton, R.W. Field, T.R. Huet, and M. Herman, "Low Energy Vibrational Levels in the $\tilde{A}^1A_u$ Electronic State of C_2D_2 ", J. Mol. Spectrosc. 137, 427-429 (1989).

Y. Chen, S.D. Halle, D.M. Jonas, J.L. Kinsey, and R.W. Field, "Stimulated Emission Pumping Studies of Acetylene $\tilde{X}^1\Sigma_g^+$ in the 11,400-15,700 cm^{-1} Region: the Onset of Mixing", J. Opt. Soc. Am. B 00, 0000-0000 (1990).

X. Zhao, G.W. Adamson, and R.W. Field, "The $\tilde{B}^2A' \leftarrow \tilde{X}^2A'$ Fluorescence Excitation Spectrum of the HCO Radical", J. Chem. Phys.

K. Yamanouchi, N. Ikeda, S. Tsuchiya, D.M. Jonas, J.K. Lundberg, and R.W. Field, "Vibrationally Highly Excited Acetylene as Studied by Dispersed Fluorescence and Stimulated Emission Pumping Spectroscopy: Vibrational Assignment of the Feature States", J. Chem. Phys.

P. Dupré, R. Jost, M. Lombardi, P.G. Green, E. Abramson, and R.W. Field, "Anomalous Behavior of the Anticrossing Density as a Function of Excitation Energy in the C_2H_2 Molecule", Chem. Phys.

END

DATE FILMED

02 / 14 / 91