UNIMOLECULAR AND BIMOLECULAR REACTIONS INDUCED BY STATE-SPECIFIC VIBRATIONAL EXCITATION

Progress Report

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MASTER

TECHNICAL PROGRESS REPORT

- Hai-Lung Dai -

Unimolecular and Bimolecular Reactions Induced by State-Specific Vibrational Excitation

Toward the goal of understanding the role of vibrational energy in chemical reactions related to energy production, we have made several advancements, in the last couple of years. They include the understanding of chemical properties of highly vibrationally excited molecules, the characterization of vibrationally excited radicals, and the development of experimental techniques to extend our ability to investigate transient and reactive chemical species.

A. Characterization of the lowest singlet state of CH_2 and CD_2

The $J \leq 7$ and $K_a \leq 3$ rotational levels of the bending vibrational overtones, (0,2,0), (0,3,0), and (0,4,0), and the (1,1,0) combination band of $\tilde{a}^1A_1$ CH_2 were characterized in detail by stimulated emission spectroscopy (SES). The methylene was generated from ketene photolysis. Spectroscopic analyses using a rigid rotor Hamiltonian gave the vibrational term values and rotational constants. The latter were found to be strongly J and K_a dependent, suggesting the inadequacy of the rigid rotor Hamiltonian for calculating the rotational energy to high accuracy. Effects of Coriolis, Fermi, and singlet-triplet perturbations were all observed in the spectra and discussed. Abnormally intense $\Delta K_a=3$ and 5 transitions were observed in the $\tilde{a} \leftrightarrow \tilde{b}$ bands. This observation has allowed the assignment of many of the previously unassignable $\tilde{b} \leftarrow \tilde{a}$ transitions. From fitting the experimentally measured bending vibrational term values by a model calculation based on the WKB theory, the barrier height to linearity in the $\tilde{a}$ state was determined to be 9870 cm^{-1} . Similar studies have been conducted for the CD_2 molecule as well.

B. Mode-specificity in $\text{H}_2\text{CO}(\text{S}_0)$ dissociation at $28,300\text{ cm}^{-1}$

In the past several years, we have used the Stark Level Crossing Spectroscopy to measure the dissociation rates of H_2CO excited at $\sim 28,300\text{ cm}^{-1}$ in vibrational energy. The measurements showed that the dissociation rates of the isoenergetic vibrational levels vary over two orders of magnitude. The most interesting questions related to this intriguing observation are what is the cause for this large variation, and does mode specificity--i.e., the levels coupled more strongly to the dissociation coordinate that dissociate faster--exist?

Since the dissociation coordinate is orthogonal to the out-of-plane bending motion and since this vibration contributes most to the $\text{S}_0\text{-S}_1$ matrix elements, which were also measured in the experiments, one assumes that mode-specificity would be manifested by a reciprocal relation between the matrix elements and the dissociation rates. However, this was not what was observed. As a matter of fact, if a correlation does exist in the experimental data, it seems to be a positive correlation, i.e., the S_0 levels that dissociate faster tend to have larger $\text{S}_0\text{-S}_1$ matrix elements. (See figure.)

Each point in the graph represents the dissociation-dominant linewidth of a high vibrational level of H_2CO $\sim 28,300\text{ cm}^{-1}$ and its matrix element with the S_1 rovibronic level.

We have recently carefully analyzed the calculation of the matrix element. It turned out that for a level with ν_{oop} approximately less than four, the matrix element increases with increasing out-of-plane quantum number in this level. ν_{oop} is the out-of-plane motion quantum number. However, for $\nu_{\text{oop}} \geq 4$, the more out-of-plane energy is in the S_0 level, the smaller the matrix element gets. For this latter situation, mode-specificity would require a positive correlation between the matrix-element and the dissociation rate. Since we surmise that the average of ν_{oop} is ≥ 4 at $\sim 28,300 \text{ cm}^{-1}$, the observation of a positive correlation between matrix elements and dissociation rates suggests that mode-specificity does exist in H_2CO dissociation.

C. Development of time-resolved Fourier transform emission spectroscopy

We have developed a new time-resolved Fourier transform spectroscopic technique that is capable of 50 nsec temporal and 0.25 cm^{-1} spectral resolution in the visible region. The time-resolved capability of the spectrometer is achieved by running the interferometer in a step-scan mode and recording the signal with real-time resolution at each mirror position. The temporal and spectral resolution was demonstrated by detecting the scattered light from a dye laser pulse and by dispersing the laser-induced fluorescence from an I_2 gas cell in the $16,000$ to $19,000 \text{ cm}^{-1}$ region. This spectrometer will allow us to observe the rovibronic transitions of transient species with high resolution. Our capability of studying the structure and spectroscopy of a transient species will be greatly advanced.

D. F_2CC identification and characterization

The success of our Flash Photolysis Stimulated Emission Pumping method in characterizing the vibration-rotation structure of CH_2 indicates that other transient radicals with optically accessible electronic transitions can be studied the same way. We have achieved preliminary success on the difluorovinylidene radical.

F₂CC is interesting for several reasons. It is a small but important freon radical. From *ab initio* calculations, it assumes the same structure as vinylidene, but unlike vinylidene it is thermally stable. A previous Russian study (Khalturin et al., *J. Gen. Chem. USSR* **58**, 1203 (1988)) in emission from a fluorocarbon plasma has claimed the observation of F₂CC vibronic transitions associated with the CF₂ rocking motion.

We have attempted to confirm these results. F₂CC is generated by photolysis of F₂CC=CO, which is synthesized by an organic group at Penn, with an excimer laser at 308 nm. Tunable laser pulses in the 470-480 nm region have been used to induce fluorescence. So far only one band centered at 21,107 cm⁻¹ has been recorded, which does not seem to match with the previously reported results. Rotational constants obtained from the band contour analysis agree with the ones calculated from the *ab initio* structure. We intend to continue the LIF study for the determination of the F₂CC structure and its electronic transitions. Stimulated emission spectroscopy will subsequently be used to characterize the vibration-rotation levels of this transient species.

E. Publications from DOE-supported project from 1989- .

Transient Vibrational Spectroscopy of $\tilde{a}^1A_1$, *J. Mol. Spectr.* **138**, 596 (1989), W. Xie, C. Harkin, H. L. Dai, W. H. Green, Jr., Q. K. Zheng, and A. J. Mahoney.

Preventing Rapid Decomposition of Rhodamine Dyes in Excimer-Pumped Pulsed Dye Lasers, *Rev. Sci. Instr.* **61**, 191 (1990), P. D. Arias and H. L. Dai.

*Bending Overtones and Barrier Height of the $\tilde{a}^1A_1$ State of CH₂ by flash Photolysis Stimulated Emission Pumping, *J. Chem. Phys.* **93**, 4615 (1990), Wei Xie, Carmel Harkin, and Hai-Lung Dai.

*Laser Vibrational Spectroscopy of Transient, Weakly Bound and Reactive Molecules, *Applied Spect.* **44**, 1595 (1990), Hai-Lung Dai.

Vibration-Rotation Spectroscopy with Dye Lasers: Higher Sensitivity and Extended Frequency Range via Stimulated Emission Pumping, *Lambda Physik Highlights* **23**, 1 (1990), Uwe Brinkmann and Hai-Lung Dai.

Vibrational Spectroscopy and Dynamics of Transient and Weakly Bound Molecules by Stimulated Emission Pumping, in "Advances in Multi-Photon Processes and Spectroscopy," ed. S. H. Lin (World Scientific, 1991), Vol. 7, 171, H. L. Dai.

*The Chemical and Physical Properties of Vibration-Rotation Eigenstates of $\text{H}_2\text{CO}(S_0)$ at $28,300\text{ cm}^{-1}$, in "Advances in Molecular Vibrations," ed. J. M. Bowman (JAI Press, Connecticut, 1991), 305, H. L. Dai.

Time-Resolved Fourier Transform Spectroscopy with 50 nsec and Time and 0.25 cm^{-1} Spectral Resolution in the visible, G. V. Hartland, W. Xie, H. L. Dai, A. Simon, and M. J. Anderson, *Rev. Sci. Instr.*, submitted.

Observation of Strong $\Delta K_a=5$ Transitions in the $\tilde{b}^1B_1 \leftarrow \tilde{a}^1A_1$ Bands of CH_2 , *J. Chem. Phys.*, submitted, W. Xie and H. L. Dai.

Vibration-Rotation Eigenstates of H_2CO at $28,300\text{ cm}^{-1}$. I. Dissociation Rates and Mode-Specificity, to be submitted to *J. Chem. Phys.*, A. Ritter, W. Merry, D. Frye, and H. L. Dai.

Vibration-Rotation Eigenstates of H_2CO at $28,300\text{ cm}^{-1}$. II. Density of States and Coriolis Coupling, to be submitted to *J. Chem. Phys.*, A. Ritter and H. L. Dai.

*These articles are attached to this report.

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