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Gas Phase Molecular Dynamics

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INTRODUCTION

The goal of this research is the understanding of elementary chemical and physical processes important in the combustion of fossil fuels. Interest centers on reactions involving short-lived chemical intermediates and their properties. High-resolution, high-sensitivity, laser absorption methods are augmented by high temperature flow-tube reaction kinetics studies with mass-spectrometric sampling. These experiments provide information on the energy levels, structures and reactivity of molecular free radical species and, in turn, provide new tools for the study of energy flow and chemical bond cleavage in the radicals in chemical systems. The experimental work is supported by theoretical and computational work using time-dependent quantum wavepacket calculations that provide insights into energy flow between the vibrational modes of the molecule. The work of group members Fockenberg and Muckerman is described in separate abstracts of this volume.

HIGHLIGHTS OF RECENT PROGRESS

(i) Infrared Spectroscopy of C_2H_5

Much progress has been made in the analysis of the infrared spectrum of C_2H_5 near 500 cm^{-1}. Hundreds of new vibration-rotation-torsion transitions have been assigned. A new absorption cell based on the Herriott configuration developed for the near-IR spectrometers was completed and new spectra recorded, following predictions from the ongoing analysis. Ethyl is the simplest alkyl radical that exhibits the torsional and low-frequency vibrational motions expected to dominate the internal dynamics of all heavier members of this radical class. We had previously recorded part of this spectrum of ethyl and reported a preliminary analysis some time ago. The new data permit good estimates of the torsional barrier in the zero-point level and its change on excitation of the CH_2 rocking (umbrella) vibration. Extensive *ab initio* calculations performed in collaboration with Prof. Philip Johnson (SUNY, Stony Brook) guided the spectral analysis and provided physical insight into the coupling between the various motions. Analysis of the spectrum leads to estimates of the torsional barrier of 16.6 cm^{-1} in the zero-point level, decreasing to 10.3 cm^{-1} on excitation of the CH_2-rocking fundamental. The electronic structure calculations provided estimates of the change in the vibrational frequencies as a function of torsional angle as well as the electronic contribution to the barrier. Together, these were used to provide purely theoretical estimates of the torsional barriers, which are 17.6 cm^{-1} and 10.9 cm^{-1} respectively, in excellent agreement with the observations.

With the spectroscopy in hand, preliminary measurements of the kinetics of ethyl radical reactions with HBr and O_2 were made in collaboration with Craig Taatjes and Eileen Clifford (Sandia, Livermore) using the BNL spectrometer. We plan further measurements at elevated temperatures in the future. Related diode laser measurements, described in more detail below, have been used to calibrate quantum yields for photochemical processes used to generate C_2H_5 for radical-radical kinetics studies.

(ii) Near Infrared Spectroscopy of Carbenes

Last year, we reported new measurements of the near infrared spectrum of CH_2, methylene, by transient frequency-modulated absorption spectroscopy. We have extended the work to the study of HCBr and its deuterated isotopomer, a species that provides an interesting contrast to CH_2 because the lowest singlet and triplet states, while separated by energies similar to those in CH_2, are reversed in their ordering. In HCBr the singlet is lower by approximately 2000 cm^{-1}. A precise determination of this quantity is one of the goals of this work. Like CH_2, HCBr has a singlet band system which extends from the near infrared through the visible and is dominated by a progression in the bending vibrational mode because of the large change in equilibrium bond angle between the two states. Unlike methylene, the rotational structure in the spectrum is free from large perturbations and thus rotational assignment is comparatively straightforward. Vibronic assignments have been the subject of uncertainty in the past due to an inability to follow the band system down to the origin region, where Franck-Condon factors are smaller and spectroscopic sources have been less powerful. With the advent of tunable near-IR diode laser-based spectrometers, this has changed and we find the origin of the band system is at 11973 cm^{-1} and 11966 cm^{-1} for HCBr and DCBr respectively.

(iii) Dynamical Studies of Photoinitiated Reactions

The barrierless unimolecular decomposition of ketene to singlet CH_2 and CO has long served as a prototype for ground-state bond-fission reactions. We have observed surprising new experimental results derived from FM Doppler spectroscopy applied to this system in a slit jet expansion. Removal of the effects of the parent energy distribution provides greatly enhanced resolution in the measured Doppler lineshapes. Measurements of CH_2 product lineshapes provide clean information on the internal energy distribution of the undetected CO partner fragment. These *correlated* product distributions can be compared to correlated state measurements from the Wodtke laboratory, and extensive related work from the Moore laboratory. Energy-dependent deviations from statistical or partially adiabatic behavior become more clear in such correlated state distributions, and provide new challenges to and tests of approximate statistical theories widely used to interpolate, extrapolate and even predict rates of relevance to combustion models.

We have used transient FM Doppler spectroscopy in a study of ICN photodissociation at several wavelengths throughout the unresolved UV absorption band. This extensively studied, but still incompletely understood, direct dissociation proceeds on several interacting potential energy surfaces. It offers an excellent opportunity for experimental and theoretical investigations of mixed adiabatic and diabatic dynamics, and coherent effects in polyatomic dissociation. Direct comparisons are being made between the semiclassical bipolar moment framework for Doppler profile analysis of polarized photofragments, and a new, explicitly coherent formalism due to Zare and co-workers. Preliminary theoretical work has uncovered an unexpected generality of the older, semiclassical formalism, which apparently makes it able to identify and quantify coherent effects. Our extensive high-resolution measurements of ICN photodissociation by FM Doppler methods will provide a rigorous test of the theoretical comparisons.

(iv) Diode Laser Probes of Combustion Kinetics

Characterization of radical-radical kinetics of combustion-related species using time-of-flight mass spectrometric detection is a major theme in our group's recent research efforts and is discussed in detail in Christopher Fockenberg's abstract. While this powerful technique offers major advantages for simultaneous detection of many species involved in reactions, it is mute concerning product internal-state distributions that can be measured on a case-by-case basis by laser spectroscopic techniques. It also relies upon knowledge of photochemical quantum yields of the laser-induced photolysis reactions used to generate the radicals under study. We have reconstructed and improved an infrared diode laser kinetic absorption spectroscopy apparatus to address these requirements.

The first results from this new effort relate to reactions of ethyl radicals. The work has been prompted by recent progress in determination of the IR absorption spectrum of ethyl radicals in our group. In preparation for a study of the reactions between ethyl radicals and O atoms, we have determined the quantum yield of CO in the 193-nm photolysis of diethyl ketone (3-pentanone, DEK), a convenient source of ethyl radicals, in order to begin quantifying the products of this reaction. The CO quantum yield is measured by comparing the intensity of the absorption of the CO P(16) $v = 0 \rightarrow v = 1$ line to the intensity of the same line produced from the 193-nm photolysis of acetone-h_6, a reaction for which the CO-quantum yield is known. The measured CO quantum yield from DEK is 0.91 ± 0.17. Evidence for a quantum yield of less than one is supported by a recent kinetics result from our group where C_2H_4 was observed as a ~20±10% product of this photolysis. We plan further work to determine whether ethylene is a primary or secondary product of the reaction.

FUTURE PLANS

The spectra of bromomethylene are very rich and contain much additional information that we have yet to extract. Preliminary rotational analysis of a band involving $v_2'' = 2$ of HCBr suggests this ground state level is perturbed, the first possible indication of the presence of background triplet state levels. Assignment of the perturbing level will allow a direct estimate of the triplet-singlet splitting. Future work on this system will also include attempts to measure rate constants for reactions of singlet bromomethylene. It will be interesting to see if this species retains the extreme chemical reactivity of singlet CH_2.

New investigations of the unimolecular dissociation of cyanogen are planned using FM Doppler spectroscopy with tunable excitation energies. We will thus be able to address general questions concerning the role of long-range anisotropic forces on "barrierless" dissociations, possible triplet state participation in the dissociation, and effects of specific selection of vibrational and total angular momentum. Subtle, but pervasive deviations from statistical models make this dissociation one whose greater understanding promises rewarding insights.

Further characterization of the 193-nm photolysis of DEK requires detection of the ethyl product. A simple method means of probing this species without encountering the limitations of lead-salt diode laser wavelengths or the complexities of the ethyl radical spectrum is to titrate C_2H_5 using its fast reaction with Cl_2 and to infer ethyl radical concentrations from the intensity of the (stable) chloroethane spectrum. This study will be undertaken shortly. We have recently incorporated a Herriott-type cell in the apparatus that will increase the spectrometer sensitivity and permit a diode-laser-based kinetic study of the rate of reaction of CD_3 radicals, produced from the 193-nm photolysis of acetone-d_6, with O atoms produced from the co-photolysis of SO_2.

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