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Vacuum Ultraviolet Spectroscopy and Dynamics

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Vacuum Ultraviolet Spectroscopy and Dynamics

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Scope of Project

The primary focus of this project is to develop and apply novel spectroscopic techniques in the UV and VUV region to the understanding of molecular dynamical processes at the microscopic level. The approach is to apply a recently developed high-resolution laser source to obtain and analyze photoionization and photoelectron spectra of jet-cooled species and of reaction products resulting from unimolecular or bimolecular dissociation processes.

Recent Progress

1. Development of Ultranarrow Bandwidth VUV-XUV Laser System. An ultra-high brightness laser system has been constructed to study spectroscopy and dynamics in the VUV and XUV spectral region. The laser utilizes pulse amplification of a single-mode ring dye laser, frequency doubling, and four-wave mixing in a pulsed jet. Pulse energies of >100 mJ in the visible and $>10^{11}$ photons/pulse in the VUV-XUV have been obtained. The bandwidth of the laser is measured to be 91 MHz in the visible and 210 MHz in the XUV.

2. Ultrahigh-resolution (1+1) Photoionization Spectroscopy of Krypton. As a first test of the new laser, we measured the hyperfine structures and isotope shifts for the Kr I n=5,6,7 $4p^5$ ns Rydberg levels in a resonant two-photon-ionization scheme. The results yield an improved absolute calibration of the Kr energy levels by more than an order of magnitude. The nuclear quadrupole hyperfine structure indicates that the $4p^5 6s$ and $4p^5 7s$ states are described by a pure jj-coupling scheme, whereas the $4p^5 5s$ state departs from a pure jj-coupling scheme by 0.36(6)%. The magnetic hyperfine structures show that the ns states are mixed with the n'd states. Lifetimes are measured for the 6s and 7s states for the first time. These lifetimes differ markedly from theoretical literature values.

3. State-selective Ionization of N_2. Ion-molecule reactions involving carbon and/or nitrogen containing ionic species can play a moderately important role in processes such as ignition of combustion engines. Information on state-specific ionic reactions is very scarce. This is largely due to a lack of methods to generate large populations of state-selected ions for reactivity studies. Photoionization of molecules which are excited to a Rydberg state is an elegant way to prepare the resulting ions in

a single vibrational state and a limited number of rotational levels. The selectivity is based on the similarity of the Rydberg and ionic potential energy surfaces. A near ideal Franck-Condon overlap leads to the conservation of the vibrational quantum number during the ionization transition. Incorporated in an efficient resonance-enhanced multiphoton ionization scheme, this technique may yield large number of well-characterized ions for ion beam experiments.

Efficient generation of N_2^+ $X^2\Sigma_g^+(\nu_+=0,1)$ is demonstrated by an XUV + visible (1+1) photon excitation scheme. The $c'_4\ ^1\Sigma_u^+$ $(\nu'=0,1)$ Rydberg states are used as intermediates. The N_2 molecules are ionized near the $\nu_+=0$ and $\nu_+=1$ ionization thresholds. The autoionizing $nd\sigma_g\ ^1\Delta_g$ Rydberg series with the rotational quantum numbers N=4,5, and 6 (in the limit of l uncoupling) are observed for the first time. Extrapolation of the N=4 series yields an improved ionization energy of N_2 of 125666.959(67) cm^{-1}.

4. Dynamics of H_2 Elimination from 1,3 and 1,4-Cyclohexadiene. In the photolysis of 1,4-cyclohexadiene (CHDN) at 193nm, it has been shown that the concerted H_2 elimination and C-H bond rupture are two primary reaction channels following internal conversion. 1,3-CHDN, on the other hand, isomerizes to 1,4-CHDN before H_2 elimination occurs. Preliminary studies have been carried out on the photodissociation dynamics of both 1,4-CHDN and 1,3-CHDN at 212nm by probing the vibrational, rotational as well as translational energy distributions in the H_2 product through a VUV-UV two photon REMPI process. The population of H_2 in each rovibrational state was determined by measuring the transition intensities of the Lyman and Werner bands. Since the transitions to the $B^1\Sigma_g^+$ or $C^1\Pi_u$ states are direct absorption processes, the state population of H_2 can be calibrated rather accurately based on the theoretical oscillator strengths and known experimental parameters.

The quantum state distributions, the translational energy distribution and the Doppler profiles were measured giving a "rotational temperature" of ~1600K, a "vibrational temperature" of ~4000K and a translational energy of ~30 kcal/mole for H_2. A very significant observation is a strong correlation of the rotational angular momentum and the recoil velocity of the H_2 fragment. Anisotropy in the Doppler profile indicates that the H_2's velocity vector is aligned parallel to its angular momentum vector. This shows a preference of the H_2 recoiling in a "helicopter" type motion from the benzene in the dissociation process.

Future Plans

1. High Resolution Photoionization Spectroscopy of Cold Polyatomic Radicals. With the development of the high resolution transform-limited VUV laser, a series of vibrational-rotational state-resolved photoionization studies of polyatomic radicals can be carried out for the first time using a supersonically cooled radical beam source. This series of experiments will be designed to obtain some urgently needed accurate thermodynamic and spectroscopic data and to investigate intramolecular dynamical processes in detail. The experiments will include the measurement of ion yield as a

function of laser wavelength, photoelectron kinetic energy spectra at a given frequency, and zero energy electron-ion coincidence spectra. IR+VUV two-photon spectroscopy will elucidate critical vibrational data of the radicals.

2. Intramolecular Dynamics of Locally Excited Molecules. In order to study the higher vibrational levels of benzene and other molecules for which C-H stretching vibrations become significantly coupled to other modes, new forms of spectroscopy must be developed which eliminate rotational structure. For v=4 and higher C-H overtones, the absorption cross sections are too small to excite a substantial fraction of molecules or for a significant fraction of photons to be absorbed. For spectroscopy of a cooled molecular beam a background-free "flop-in" experiment is needed in which a signal is produced only when light of the proper frequencies interacts with the molecules. A three-step ir+vis+vuv photoionization will provide a detectable ion signal. There should be sufficient discrimination between ionization of rotationally-selected vibrationally-excited molecules and ground state molecules (about eight orders of magnitude) to provide an acceptably low background. This should provide a generally useful method for high overtone spectroscopy of many molecules including benzene.

3. H_2 Elimination Dynamics of Ethylene. The photodissociation dynamics of ethylene will be studied by carrying out state-specific detection of the H_2 product via (1+1) REMPI. Ethylene has two possible channels for H_2 elimination: H_2 + C=CH_2 and H_2 + HC=CH. These channels will be examined independently through the use of deuterium labelled compounds. This will enable us to make a comparison between the dynamics of H_2 elimination from a three-centered and a four-centered transition state. H_2 state distributions, kinetic energy release and the possible polarization of H_2 rotational angular momentum with respect to the relative velocity vector will provide valuable information on the nature of the transition states of H_2 elimination from ethylene.

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Research Publications.

1. T. Trickl, M.J.J. Vrakking, E. Cromwell, Y.T. Lee, and A.H. Kung, Ultrahigh-Resolution (1+1) Photoionization Spectroscopy of KrI: Hyperfine Structures, Isotope Shifts and Lifetimes for the n=5,6,7 $4p^5ns$ Rydberg States, Phys. Rev. A **39** 2948-2955 (1989). LBL-25787

2. E. Cromwell, T. Trick, Y. T. Lee, and A. H. Kung, Ultra-Narrow Bandwidth VUV-XUV Laser System. Rev. Sci. Instrum. **60**, 2888-2892 (1989). LBL-26041

3. T. Trickl, E. Cromwell, Y.T. Lee, and A.H. Kung, State-Selective Ionization of Nitrogen in the $X\ ^2\Sigma_g^+ v^+ = 0$ and $v^+ = 1$ States by Two-Color (1+1) Photon Excitation Near Threshold. J. Chem. Phys. **91**, 6006-6012 (1989). LBL-27186

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