III-G Time-Resolved Photoelectron Imaging on Ultrafast Chemical Dynamics

We have developed a novel experimental technique of time-resolved photoelectron imaging to probe excited state dynamics of isolated molecules and clusters in real time [*J. Chem. Phys.* **111**, 4859 (1999)]. A pump pulse prepares a non-stationary state in the excited electronic state, then a probe pulse projects the wavefunction to the cationic states. With a 1 kHz laser system, one electron image can be recorded for less than a minute, which allows us to map out excited state dynamics quite rapidly.

III-G-1 Femtosecond Time-Resolved Photoelectron Imaging on Ultrafast Dephasing in Pyrazine

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Femtosecond time-resolved photoelectron imaging was applied to ultrafast electronic dephasing in Pyrazine that is the best-known example of an intermediate coupling case in radiationless transition. A tunable pump pulse in 300 nm range prepared Pyrazine molecule in a variety of vibronic levels in $S_1(\pi,\pi^*)$, and the subsequent time-evolution has been probed by either one photon ionization at 197 nm or two-photon ionization at 395 nm. The decay of the optically-prepared S_1 character and the corresponding formation of the T_1 character were clearly observed in both probing schemes. The photoelectron kinetic energy distribution in (1+1') ionization exhibited clear vibrational structure that is essentially determined by Franck-Condon factors between the S_1 and cationic state. For any of the S_1 vibronic levels up to the excess energy of 2000 cm^{-1}, no signature of IVR has been observed in the photoelectron images. On the other hand, (1+2') ionization provided a few sharp lines in the kinetic energy distribution due to the accidental resonance with the 3s and 3p Rydberg states at (1+1') energy. The photoelectron angular distribution in (1+2') ionization exhibited high anisotropy, which proves that the atomic-like electron orbital is involved in the resonant state.

III-H Crossed Beam Studies on Bimolecular Reaction Dynamics

Chemical reactions under thermal conditions occur with various collision energies, internal quantum states, and impact parameters. The experimental data measured under such conditions are highly-averaged quantities, from which detailed feature of reactions can hardly be learned. A crossed molecular beam method allows us to observe chemical reactions of state-selected reagents at well-defined collision energy. Although, this method does not control the impact parameter in reaction, the differential cross section (angular distribution of products) reveals impact-parameter dependence of reaction probability and reaction mechanism. Conventional crossed beam experiments have employed so-called a universal detector (electron bombardment + quadrupole mass analysis + time-of-flight measurements). However, this method provides poor (or no) internal state resolution of products. The internal motions (electronic, vibrational and rotational) of molecules play essential roles in chemical reactions, therefore the measurements of only the scattering distributions are generally insufficient for elucidation of reaction mechanism. We constructed a new crossed beam apparatus with a high-resolution ion imaging detector. The products are state-selectively ionized by resonantly enhanced multiphoton ionization (REMPI) and their scattering distributions are directly visualized by an imaging method. The state-selective detection diminishes the signal intensity, but this is compensated by simultaneous observation of all the scattering angle. A preliminary experiment on the inelastic scattering of NO with Ar achieved the data acquisition more than two orders of magnitude faster than previous methods. A photolytic $O(^1D)$ atomic beam source has also been constructed to study stratospheric chemistry at the state-to-state differential cross section level.

III-H-1 State-Resolved Differential Cross Section Measurements for the Inelastic Scattering of NO + Ar

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The state-resolved differential cross sections (SR-DCS) of the inelastic scattering NO (j" = 0.5, Ω" = 1/2) + Ar → NO (j', Ω' = 1/2, 3/2) + Ar at 63 meV were measured by a crossed molecular beam ion-imaging method. The dynamics of this system occurs on the two potential energy surfaces that arise from the approach of Ar to NO in the $^2\Pi$ state, and the average and difference potentials of these two determine the spin-orbit changing ($\Delta\Omega = 1$) and conserving transitions ($\Delta\Omega = 0$). Many workers have studied NO + Ar both theoretically and experimentally as a representative system of inelastic scattering of open-shell molecules. In our experiment, twenty final (j', Ω') states in total were observed for both spin-orbit conversing (Ω" = 1/2 → Ω' = 1/2) and changing (Ω" = 1/2 → Ω' = 3/2) processes. The DCSs exhibited complex structures that are sensitive to the final (j', Ω') states; sharp forward scattering for low j' states, broad angular distributions for intermediate *j'* states, and backward scattering for high *j'* states. The results were in excellent agreement with close-coupling calculations on the CCSD(T) surfaces performed by Millard Alexander at Maryland University.

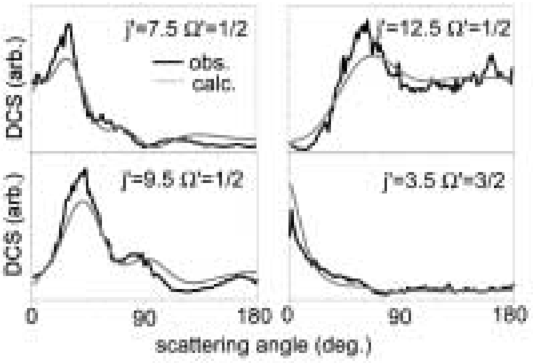

Figure 1. The observed and calculated state-resolved differential cross section of the inelastic scattering of NO + Ar. The final states of scattered NO are denoted as (*j'*, Ω').

III-I Non-Adiabatic Molecular Photodissociation Dynamics Studied by Polarization Spectroscopy

Vector quantities of products provide detailed insights into the stereochemical dynamics of atomic/molecular collisions and molecular photodissociation. As expected from building-up principle of diatomic molecule, the ***orbital alignment*** and ***orientation*** in an atomic fragment carries information on the electronic symmetry of the PES. Furthermore, coherent excitation leading to two different dissociation paths creates characteristic vector correlation.

III-I-1 Atomic Orbital Orientation in Photodissociation of OCS

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The orbital orientation of S($^1D_2$) was detected in photodissociation of OCS by an ion imaging technique with circularly-polarized probe light. One of the causes for orientation is quantum mechanical interference between the two different dissociation pathways reached by parallel and perpendicular transitions. The magnitude of the orientation is proportional to the asymptotic phase difference between the pathways, making the orientation to be a sensitive probe of the potential energy surfaces. The S($^1D_2$) products consist of two components arising from a mixed transition to $2^1A'$, $1^1A''$ and from a pure parallel transition to $2^1A'$. The former appears with high translational energy of 12.7 kcal/mol and the latter 3.8 kcal/mol. As shown in Figure 1, the signal of high energy component showed strong orientation.

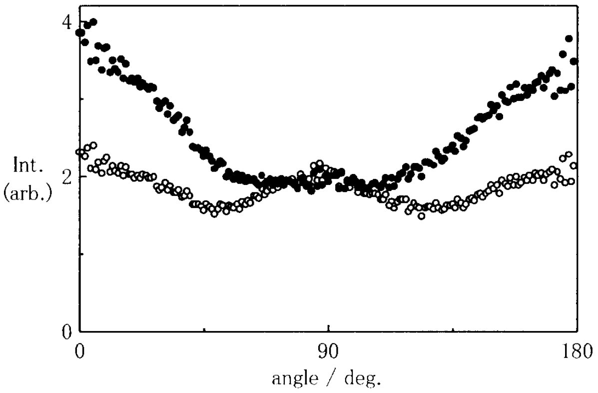

Figure 1. Angular distributions of high and low energy S^+ ions created by linearly polarized 235 nm pump light, and the right (●) left (○) circularly polarized probe light. Definition of θ is illustrated in the figure. ε_{dis} and s_{pr} are polarization vectors of the pump light and a helicity vector of the probe, respectively.