III-E Femtosecond Time-Resolved Photoelectron Imaging

Photodissociation dynamics has been studied extensively by measuring quantum state and scattering distributions of products. However, the most unambiguous experimental elucidation of reaction mechanism is by real-time observation of the reaction. Photoelectron spectroscopy is useful for this purpose, since it projects the wavepacket dynamics in the excited state to an accurately-known cation potential. Other advantages of photoelectron spectroscopy are (1) capability of detecting both singlet and triplet states, enabling direct observation of intersystem crossing and internal conversion processes, (2) high sensitivity due to efficient collection of electrons by electromagnetic fields, and (3) applicability of ultrafast laser with fixed wavelength. The analysis of photoelectron scattering distribution has been performed most often by the time-of-flight (TOF) method. However, a standard TOF method has a poor collection efficiency of electrons. The magnetic bottle spectrometer significantly improved the efficiency, but angular resolution is sacrificed. Photoelecton imaging (PEI) achieves the highest collection efficiency of electrons while providing routine measurements of speed and angular distributions. This work presents PEI coupled with femtosecond pump-probe technique, for the first time.

III-E-1 Femtosecond Time-Resolved Photoelectron Imaging on Ultrafast Electronic Dephasing in an Isolated Molecule

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The femtosecond time-resolved photoelectron imaging is reported for the first time. The method was applied to ultrafast dephasing in an intermediate case molecule Pyrazine. Figure 1 shows the snapshot of photoelectron scattering distribution measured as a function of pump-probe time delay. The decay of the optically-prepared S_1 character (the outer ring) and the build-up of dark triplet character (the inner ring) are clearly seen. The result also suggests the possibility that intersystem crossing is mediated by $T_2(\pi,\pi^*)$ state. This work is the first direct observation of the dynamics in the triplet manifold of this benchmark system.

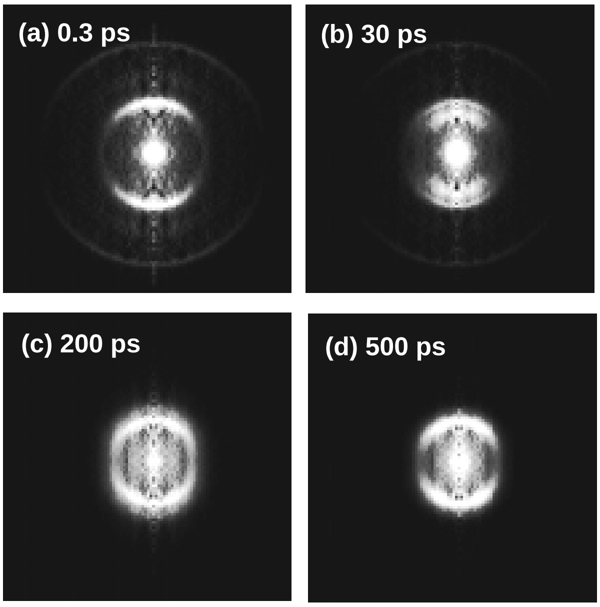

Figure 1. Inverse Abel transforms (512 × 512 pixels) of photoelectron images of [1+2'] REMPI of Pyrazine via the $S_1[^1B_{3u}(n,\pi^*)]$ 0^0 level at the time delays of (a) 0.3, (b) 30, (c) 200, and (d) 500 ps. The original images were integrated for 36 000 laser shots.

III-F Dynamical Stereochemistry

Stereodynamics in molecular photodissociation is investigated experimentally and theoretically. Efforts are made to determine multipole moments (density matrix) of a photofragment completely and interpret them quantum-mechanically.

III-F-1 Vector Correlation in Molecular Photodissociation

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The quantum mechanical expression for the angle-dependent photofragment multiple moments is rigorously derived with only the dipole approximation. The angular momentum coupling between the two fragments is taken into account for the first time. The result is also compared with the *formal expansion method* assuming fixed $\boldsymbol{\mu}$-$\boldsymbol{v}$-$\boldsymbol{J}$ vector correlation for all scattering angles [Y. Mo and T. Suzuki, *J. Chem. Phys.* **108**, 6780 (1998)]. The condition that reduces the rigorous formula to the approximate formula is examined.