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Elucidation of the ultraviolet photodissociation dynamics of allyl iodide (C_3H_5I)

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The ultraviolet (UV) photodissociation of the allyl halides (C_3H_5X) provides a convenient source of the allyl radical (C_3H_5), which is an important species for the studies of spectroscopy, dynamics and reaction kinetics. Of the C_3H_5X, allyl iodide (C_3H_5I) shows the prototypical photochemistry because the C-I bond fission is governed by the large spin-orbit splitting between I ($^2P_{3/2}$) and I^* ($^2P_{1/2}$). The two UV absorption bands centered at 220 and 270 nm are assigned to the electronic transitions to the several excited states adiabatically correlating to the product pathways of $C_3H_5I + h\nu \rightarrow C_3H_5 + I$ or I^*. In our previous study, it was found that I^* is preferentially produced at both absorption bands and the parallel-type electronic transitions to the excited states dominate. Further detailed understanding of the reaction mechanisms including the secondary process [1] is expected to be obtained from the accurate C_3H_5 internal energy distributions with these two product pathways resolved.

In the present study, we have carried out the pump-probe experiment of C_3H_5I at photolysis wavelengths of 213 and 266 nm. The state-resolved scattering distributions of the photofragments were obtained by ion-imaging coupled with the resonantly-enhanced multi-photon ionization (REMPI) spectroscopy [2]. The velocity distributions were extracted from the scattering images of the atomic iodine (Fig) with the precisely calibrated velocity. The C_3H_5 internal energy was calculated from the I- and I^*-velocity distributions by using the conservation laws of energy and momentum. The internal energy distribution of C_3H_5 generated in the I channel at 213 nm indicates that most of C_3H_5 have a sufficient energy for the secondary decomposition ($C_3H_5 \rightarrow C_3H_4 + H$, $C_3H_5 \rightarrow C_2H_2 + CH_3$).

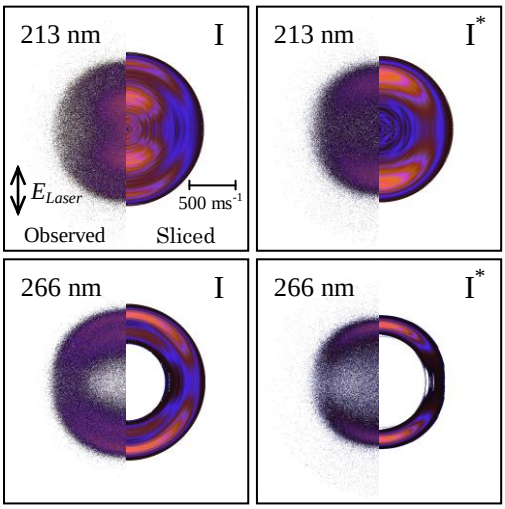

Fig Observed spin-orbit state-resolved scattering images of I and I^* produced in the photolysis of C_3H_5I at 266 nm and 213 nm.
(Left) Observed projection image
(Right) Sliced distribution

References

[1] H. Fan and S. T. Pratt, *J. Chem. Phys.* **125**, 144302 (2006)
[2] A. T. J. B. Eppink and D. H. Parker, *J. Chem. Phys.* **109**, 4758 (1998)