

# Spin-orbit Branching in Photodissociation of Allyl Iodide at 266nm and 213nm

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Allyl iodide ( $C_3H_5I$ ) is known to efficiently produce the allyl radical ( $C_3H_5$ ) by UV photoabsorption;<sup>1</sup>  $C_3H_5I + h\nu \rightarrow C_3H_5 + I(^2P)$ . The absorption spectrum of  $C_3H_5I$  has two strong and broad dissociative peaks centered at 220 nm and 270 nm. The upper electronic states of these transitions correspond to the  $^3Q_1$ ,  $^3Q_0$  and  $^1Q_1$  repulsive potential energy surfaces. The  $^3Q_1$  and  $^1Q_1$  surfaces are adiabatically correlated to the product channel of the  $C_3H_5 + I(^2P_{3/2})$ , while the  $^3Q_0$  state to the  $C_3H_5 + I^*(^2P_{1/2})$ . The spin-orbit splitting between I and  $I^*$  (0.943 eV) has significantly large portion in the available energy of UV photodissociation (2.27 eV at 266 nm), so that the dissociation dynamics is well characterized by the spin-orbit branching. The branching ratio is contributed both from photoabsorption cross-section of the adiabatic electronic states and the non-adiabatic transition probability between them.<sup>2</sup> These factors can be experimentally determined by measurement of the final state distribution and the scattering distribution.

We have carried out the pump-probe experiment of  $C_3H_5I$  at photolysis wavelength of 266 nm and 213 nm. Photofragments of atomic iodine in the different spin-orbit states ( $^2P_{3/2}$  and  $^2P_{1/2}$ ) were detected using [2+1] resonantly-enhanced multiphoton ionization (REMPI) spectroscopy. At the both photolysis wavelength,  $I^*(^2P_{1/2})$  was found to be preferentially produced. We measured the spin-orbit state-resolved scattering distribution by the ion-imaging method combined with REMPI spectroscopy. The observed angular distribution at 266 nm photolysis showed the positive anisotropy (fig.1), while the 213 nm absorption band yielded rather isotropic scattering distribution (fig.2). Under the axial recoil approximation, these angular distributions indicates that the strong 220 nm band and the weak 270 nm band have the electronic characters of the  $^3Q_1 + ^3Q_0$  and the  $^1Q_1$  states, respectively. The translational energy distribution obtained from the scattering images provided the internal energy distribution of the allyl radical associated to the  $I(^2P_{3/2})$  and  $I^*(^2P_{1/2})$  channels.

These two distributions were qualitatively similar. The similarity of the energy disposal into  $C_3H_5$  suggests the non-adiabatic transition efficiently occurs at the exit stage of the dissociation.

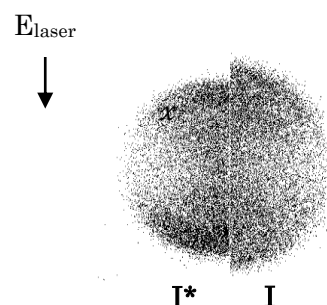


Fig.1 Scattering distribution of I and  $I^*$  in the photodissociation of  $C_3H_5I$  at 266nm

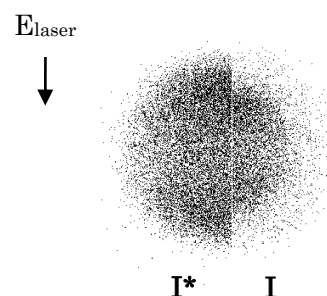


Fig.2 Scattering distribution of I and  $I^*$  in the photodissociation of  $C_3H_5I$  at 213nm

## 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**, 4767 (1998).