Site and Isotopic Effects on the Angular Anisotropy of Products in the Photodissociation of Ethene at 157 nm

Shih-Huang Lee (李世煌)[1] and Yuan T. Lee (李遠哲)[2]

[1]National Synchrotron Radiation Research Center, Hsinchu, Taiwan
[2]Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei, Taiwan

We measured TOF spectra of fragments upon photolysis of ethene in five isotopic forms using dissociating light with linear polarizations at 0^o (//) and 90^o ($\perp$) relative to the detection axis. Figure 1 shows // and $\perp$ TOF spectra of products at *m/z* = 2–4 and 26–28 after photolysis of 1,1-CH_2CD_2 and isotopomers. The rapid component of ethyne correlates with molecular hydrogen and the slow component is due to loss of two hydrogen atoms. Figure 1 indicates that two momentum-matched products, ethyne and molecular hydrogen, have the same behavior in the difference between // and $\perp$ TOF spectra, which confirms the accuracy of the measured β values. Ethyne due to loss of two hydrogen atoms has an isotropic angular distribution, independent of isotopic variants of ethene. Figure 1 also shows // and $\perp$ TOF spectra of products at *m/z* = 2, 3 and 4 from photolysis of 1,2-cis-CHDCHD and 1,2-trans- CHDCDH; these spectra were recorded using ionizing photons at 17.0 eV. The TOF spectra of atomic D were measured separately with ionizing photons at 14.0 eV. TOF spectra of H_2 are thus obtained on subtracting the 14-eV spectra from the 17-eV spectra recorded at *m/z* = 2 but not shown here.

The angular distribution of a product with a specific kinetic energy is expressible as

$$I_{cm}(E_t,\theta) = \frac{1}{4\pi} P(E_t)[1 + \beta(E_t)P_2(\cos\theta)] \qquad (1)$$

in the center-of-mass (c.m.) frame. $P(E_t)$ is the distribution of c.m. kinetic energy of product, and $\beta(E_t)$ is the distribution of the angular-anisotropy parameter as a function of E_t. E_t is the c.m. kinetic energy of products including two momentum-matched fragments. $P_2(\cos\theta)$ equals $(3\cos^2\theta - 1)/2$; θ is the angle between the recoil direction of a product and the linear polarization of the dissociating radiation. Using a computer program PHOTRAN based on forward convolution, we derived the $I_{cm}(E_t,//)$ and $I_{cm}(E_t,\perp)$ spectra from the // and $\perp$ TOF spectra, respectively. $\beta(E_t) = 2[I_{cm}(E_t,//)-I_{cm}(E_t,\perp)] / [I_{cm}(E_t,//)+2I_{cm}(E_t,\perp)]$ is derivable from eq. 1. Figure 2 summarizes $\beta(E_t)$ for elimination of molecular hydrogen from three dideuterated species of ethene. After photolysis of 1,1-CH_2CD_2, the angular anisotropy of products from dissociation into $C_2D_2 + H_2$, $C_2HD + HD$, and $C_2H_2 + D_2$ has negative, nearly zero and positive β values, respectively, which differs from the results of photolysis of 1,2-cis-CHDCHD and 1,2-trans-CHDCDH. The latter two have similar angular distribution of products; the elimination of molecular hydrogen has a negative β value and the anisotropy has a trend $D_2 > H_2 > HD$. The elimination of H_2 from C_2H_4 has a negative β value whereas the elimination of D_2 from C_2D_4 is isotropic.

The averaged β value of products ranges from –0.17 to 0.10, depending on dissociation pathways. The photolysis of dideuterated ethene reveals site and isotopic effects on the angular distributions of products; products H_2, HD and D_2 from photolysis of 1,1-CH_2CD_2 have negative, nearly zero and positive values of β, respectively. Molecular hydrogen from photolysis of 1,2-cis-CHDCHD has a negative β value and the anisotropy has a trend $D_2 > H_2 > HD$. Photolysis of 1,2-trans-CHDCDH produced a result similar to photolysis of 1,2-cis-CHDCHD for the angular anisotropy of molecular hydrogen except slightly more isotropic. A calculation of optimized geometries of ethene in the ground electronic state and pertinent transition structures enables a qualitative interpretation of the site and isotopic effects on the angular anisotropy of products. We deduce that the photo-excited state of ethene at 157 nm has a major character $^1B_{1u}$ that produces a transition dipolar moment parallel to the C=C bond.

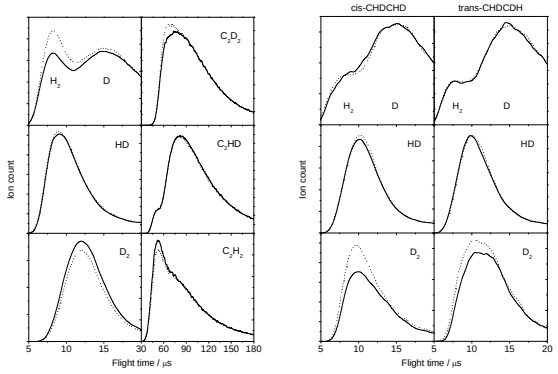

Figure 1. TOF spectra of products at *m/z* = 2, 3, 4, 26, 27 and 28 after photolysis of 1,1-CH_2CD_2, cis-CHDCHD, and trans-CHDCDH.

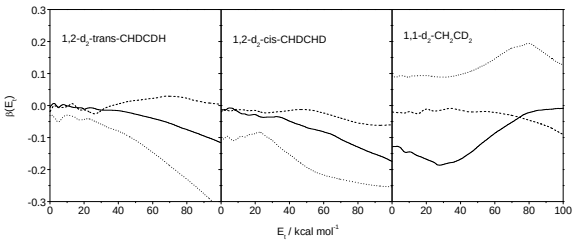

Figure 2. $\beta(E_t)$ for dissociation of $C_2D_2 + H_2$ (solid line), $C_2HD + HD$ (dashed line) and $C_2H_2 + D_2$ (dotted line) from ethene in three dideuterated variants.