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# Photodissociation dynamics of ethylene sulfide at 193.3 nm

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We have investigated the photodissociation dynamics of ethylene sulfide (thiirane) at 193.3 nm by studying Doppler broadened laser induced fluorescence spectra of atomic sulfur fragments. The only dissociative channel found produces  $S(^1D)$  atoms and ethylene molecules. The measured average translational energy of the fragments is  $20.5 \pm 4.5$  kcal/mol. We have found an anisotropy in the velocity distribution of the atomic sulfur fragments  $(\beta = 1.03 \pm 0.19)$ , which confirms that the 193 nm transition is a parallel transition. We conclude that the dissociation is direct and symmetric, both C-S bonds breaking at once. The dissociation time is estimated to be about 300 fs.

## INTRODUCTION

Studying energy disposal among photofragments is essential to understanding photodissociation dynamics of polyatomic molecules. Measurements of angular as well as translational and internal energy distributions of the fragments allow us to describe the excited state of the molecule and the dissociation process in detail. For the past several years, a great many studies on the photodissociation of polyatomic molecules have been reported.<sup>1</sup> Since the energies have to be measured in a state specific manner, these studies have been mostly done on small molecules which produce atoms or diatomic molecules as the fragments. In addition, molecules of high symmetry have been preferred in order to make theoretical descriptions less complicated. However, a detailed understanding of the process in small molecules should help to predict the behavior of larger polyatomics.

We report here a study of the photodissociation dynamics of ethylene sulfide at 193.3 nm. Ethylene sulfide is highly symmetric ( $C_{2v}$  point group), which makes the molecule a good candidate for applying knowledge obtained from studies of small molecules. If we know the structure of the molecule in the excited state and how fast the dissociation occurs, the internal energy distribution among vibrational modes in ethylene fragments can be successfully modeled using certain approximations. In addition, electronic absorption spectra of ethylene sulfide have been extensively studied and a series of Rydberg transitions have been observed in the ultraviolet (UV) and vacuum UV (VUV) region of the spectrum.<sup>2,3</sup> A recent study of electronic dichroism spectra in the region of 180-230 nm has assigned the 193 nm transition as the  $4p_{\pi} \leftarrow 3p_{\pi}$  Rydberg transition whose transition dipole is parallel to the molecular symmetry axis.<sup>4</sup>

Detection of atomic sulfur fragments from ethylene sulfide was achieved using a laser induced fluorescence technique.<sup>5,6</sup> As will be shown,  $S(^{1}D)$  is the only sulfur atom product from 193 nm dissociation:

 $C_2H_4S \rightarrow C_2H_4 + S(^1D), \quad \Delta E = 84 \text{ kcal/mol.}$ 

If we consider the photon energy at 193.3 nm (148 kcal/mol), this channel leaves about 64 kcal/mol of available en-

ergy to be distributed among various degrees of freedom of the fragments. We have measured the average translational energy of the system, which is 20.5 kcal/mol. We have also found anisotropy in the angular distribution of the sulfur fragments, which shows that the dissociation is fast and the molecule retains its molecular symmetry throughout the dissociation process.

#### EXPERIMENT

This experiment was done in a conventional pumpprobe-type apparatus. A few milliTorr of the sample was introduced into a flow cell and the 193.3 nm light from an ArF excimer laser (Lumonics HyperEx-400) dissociates the molecules. The dissociating light was polarized by placing eight brewster angled quartz plates in the output of the laser; its polarization could be rotated by 90° using a half-wave plate. The predicted polarization for this wavelength is 95%. The probe laser light (Lambda Physik EMG201 XeCl excimer laser pumped frequency doubled Lambda Physik FL3002 dye laser with Rhodamine 6G), tuned to the two photon transition of  $S(^{1}D)$  to  $S(^{1}F)$  at 288.2 nm, is introduced with a tight focus at a right angle to the dissociating light. We have used an angle tuned intracavity etalon in the probe laser in order to obtain high resolution spectra. The resolution of our doubled light is about  $0.08 \text{ cm}^{-1}$ . The VUV fluorescence was focused onto a solar blind photomultiplier tube (EMR 542G-08-17) which is oriented perpendicular to the plane of the two lasers and the signal was averaged with a boxcar average (PAR model 162). Baffles of various sizes were used to minimize the scattered laser light and optimize the signal. The spectra were recorded with a multichannel scaler and stored in a LeCroy 3500 computer.

We have varied the laser power, sample pressure, and the delay time between the two lasers in order to make sure that we maintain no collision and no saturation conditions throughout the experiment. Typical experimental conditions were: about 20 mTorr of the sample, a delay time of about 100 ns with an energy of 700  $\mu$ J/pulse of the probe light. The energy of the probe light was kept constant by adjusting the angle of the crystal while monitoring a small portion of the doubled beam with photodiodes. Ethylene sulfide obtained from Aldrich was used without further purification.

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### **RESULTS AND ANALYSIS**

Detection of atomic sulfur fragments from ethylene sulfide was achieved using the Doppler broadened laser induced fluorescence technique.  $S({}^{3}P)$  atoms were not found by LIF although they could be detected as fragments of  $CS_2$  dissociation at the same (193 nm) wavelength. No emission from  $S({}^{1}S)$  was observed, either. Therefore, we conclude that the only state of the atomic sulfur fragments is  ${}^{1}D$ .

Doppler spectroscopy on photodissociation dynamics has been thoroughly reviewed in many articles.<sup>1,7,8</sup> In brief, the average speed and velocity distribution of the fragments will give important information on the dynamics of the process. If the lifetime of the excited molecule is short compared to its rotational period, the angular distribution of the fragments depends only upon the orientation of the parent molecule. Because the absorption probability is maximum when the transition dipole is aligned parallel to the electric vector of the exciting light, we can obtain the angular distribution of the fragments along a certain direction by properly choosing the experimental geometries. In Fig. 1, a typical pair of Doppler broadened fluorescence spectra of the sulfur fragments from ethylene sulfide are shown for perpendicular and parallel polarization of the dissociating light with respect to the probe direction. The electronic transition dipole of ethylene sulfide at 193 nm has been shown to be parallel to its molecular symmetry axis.<sup>4</sup> Thus we expect that the Doppler shift should be maximized for the parallel and minimized for the perpendicular polarization provided the lifetime of the excited molecule is short.

If we assume that all sulfur atoms no matter what their speed v have the same velocity anisotropy, then the velocity distribution function  $f(v, \cos \theta)$  is

$$f(v,\cos\theta) = g(v) \left[ 1 + \beta P_2(\cos\theta_{z,\epsilon}) P_2(\cos\theta_{z,v}) \right], (1)$$

where  $\beta$  is the anisotropy parameter,  $P_2$  is the second order Legendre function, and g(v) is the speed distribution function. In Eq. (1),  $\theta_{z,\epsilon}$  and  $\theta_{z,v}$  are the angles between the probe direction and the electric vector of the dissociating





light and the fragment recoil direction, respectively. From the ratio of the second moments of the velocity distributions obtained from the Doppler broadened frequency spectra, we can obtain a value of  $\beta$ , which is

$$\beta = 5 \frac{\langle v_z^2 \rangle - \langle v_x^2 \rangle}{\langle v_z^2 \rangle + 2 \langle v_x^2 \rangle}, \qquad (2)$$

where  $\langle v_z^2 \rangle$  is the second moment obtained from the distribution along the probe axis (parallel polarization). We found the anisotropy parameter  $\beta$  is 1.03  $\pm$  0.19 from the distributions in Fig. 1.

We also measured the average kinetic energy  $\langle E \rangle$  of the sulfur fragments from the second moment of the distribution. We found  $\langle E \rangle$  to be  $11.0 \pm 0.8$  kcal/mol, which in turn gives the relative kinetic energy of the system as  $20.5 \pm 4.5$ kcal/mol from energy and angular momentum conservation. Detailed computing procedures are described in the previous paper.<sup>9</sup> The widths of our spectra shown in Fig. 1 are the result of a convolution of the bandwidth of the probe laser with the actual Doppler width of the spectra. Thus, considering our laser bandwidth of 0.08 cm<sup>-1</sup> and the two photon absorption needed for the fluorescence, we expect that the measured  $\langle E \rangle$  is somewhat larger than the actual energy. The estimated difference is about 10% if we assume the laser band is Gaussian.

#### DISCUSSION

The velocity distribution obtained from the spectra reveals the dynamics of the process. The dissociation is found to be direct and the molecule retains its molecular symmetry in the excited state as evidenced by the anisotropy in the velocity distribution of the fragments. If the dissociation were stepwise, that is by formation of an open ring radical first, which then dissociates, the parent molecule would lose its initial orientation. As a consequence, the resulting fragment distribution would be close to isotropic. Regarding the anisotropy, we expect a value of  $\beta$  of 2 for the parallel and -1 for the perpendicular polarization with axial recoil of



FIG. 2. Calculated  $\beta$  for a prolate symmetric top polyatomic molecule (C/A = 2.33) with transition dipole or dissociation direction along the symmetry axis as a function of  $\tau^* = \omega \tau$  where  $\tau$  and  $\omega$  are the lifetime and the angular velocity of the excited molecule, respectively.



FIG. 3. Absorption spectrum of ethylene sulfide (reprinted from Ref. 11).

the fragments. Our measured  $\beta$  indeed indicates the transition at 193 nm is a parallel transition, although we measure a smaller value of  $\beta$  than 2. There could be several reasons. In the first place, as we expect in polyatomic molecules, there should be an internal energy distribution of the other fragments which results in a wide range of speeds in the atomic sulfur fragments. Therefore, the measured distribution is the average of individual distributions of different speeds which are double peaks with different widths for the parallel polarization. The wide speed distribution as well as the resolution of our probe laser affects the shape of the distribution and the value of the second moments. As a result, we obtained a flat top at the center of the spectrum as shown in Fig. 1. The fact that the dissociating light was not 100% polarized also reduces the experimental  $\beta$ . In the second place, as the dissociation is not instantaneous, the molecule may rotate through a small angle before the fragments separate. This could be due to the room temperature thermal rotation as well as any rotation generated by the dissociation.

According to the theory of Yang and Bersohn, the lifetime of the excited molecules can be estimated from  $\beta$  and the molecular rotational period.<sup>10</sup> A general form of  $\beta$  for rotating molecules was obtained by averaging over the distribution of initial orientations of the excited molecules. For a symmetric top with the transition dipole or dissociation direction along the symmetry axis, the calculated  $\beta$  as a function of the dimensionless quantity,  $\tau^* = \omega \tau$  is shown in Fig. 2 for C/A = 2.33, where A and C are the rotational constants along and perpendicular to the principal axis,  $\omega$  is the rms angular velocity, and  $\tau$  is the lifetime of the excited molecule. Because the two transverse moments of inertia of ethylene sulfide are very similar, it is close to a symmetric top. We obtained  $\tau^* \sim 0.5$  from our experimental  $\beta$  of 1.03, which gives an estimated lifetime of the excited molecule about ten times shorter than the rotational period, that is, about 300 fs. In turn, this implies an intrinsic width of the Rydberg transition of  $100 \text{ cm}^{-1}$ .

The optical spectrum (Fig. 3) shows that the absorption in question appears to be a typical sharp Rydberg transition about 1 nm wide [full width at half-maximum (FWHM)] which is an order of magnitude more intense than the adjacent continuous absorption. According to Clark and Simpson the Rydberg peak is centered at 193.5 nm.<sup>11</sup> Thus there is substantial overlap of the absorption with the emission of the ArF laser which peaks at 193.3 nm. We cannot, unfortunately, tune the ArF laser through the absorption peak but are convinced that the good signal/noise in the experiment is possible only because of the overlap; in other words the background absorption is too weak to produce the observed signal.

There is an apparent paradox between the sharp Rydberg transition to a quasistable excited state and the fact that the dissociation appears to be direct. The paradox is resolved by assuming that the Rydberg state is mixed with a dissociative state to a degree not previously realized. This conclusion may be a very general one. Note also that no fluorescence is observed following absorption at 193 nm showing that nonradiative transtions take place on the picosecond or subpicosecond time scale.

The average kinetic energy of the system was measured to be 20.5 kcal/mol which leaves 43.5 kcal/mol of the available energy as the internal energy in the ethylene fragments. Since the dissociation is direct and fast, the molecule would retain its  $C_{2v}$  symmetry throughout the dissociation, which makes the center of mass of the molecule remain on the dissociation axis. As a result, we expect that most of the available energy is distributed in vibrational modes rather than in rotational degrees of freedom of the ethylene. Assuming a thermal energy distribution among all the vibrational modes, we obtain the internal temperature of the ethylene at 2900 K. The vibrational excitation has two causes. First, there is a large repulsive force between the two fragments which gives the ethylene molecule an average kinetic energy of 11 kcal/mol. Even more important is the fact that the  $C_2H_4$  moiety of the ethylene sulfide molecule is a grossly distorted ethylene. The C-C bond distance is 1.48 Å compared to 1.32 Å and the CH<sub>2</sub> plane makes an angle of 152° with the C-C bond as compared to 180° in ethylene. According to the Frank-Condon principle, much of the departing ethylene should be strongly excited in the C–C stretch  $(v_2)$  because there is insufficient time for relaxation during the dissociation. In general, because the  $C_{2\nu}$  symmetry is preserved during the dissociation, only those modes of type  $a_1$  and  $C_{2\nu}$  or even quanta of the other modes would initially be excited.

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