Photodissociation Dynamics of H_2S at 243 nm: Translational Anisotropy of the Fragments Measured by Doppler Broadened H Atom Spectra

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Received December 7, 1998

Studies of photodissociation dynamics of H_2S excited within the first continuum have been reported by many authors. The absorption starts from around 250 nm and peaks about 200 nm with diffuse bands at shorter wavelengths superimposed by broad continuum.[1] In the earlier studies, internal energy distributions of the SH fragments at various photolysis wavelengths within the first continuum were measured by laser induced fluorescence and by H atom photofragment translational spectroscopy.[2~6] Angular distribution of the fragments was measured by the H atom ion signals at various polarization directions of the photolysis light with respect to the detection axis of the TOF mass spectrometer. The dissociation dynamics was also studied by measuring emission spectra of dissociating H_2S molecules.[7,8] The measured vibrational distribution is largely peaked at v=0 but significant populations are found at the excited vibrational states up to v=6. The degree of vibrational excitation is decreased as the photolysis wavelength is increased. The measured translational anisotropy parameters at various photolysis wavelengths reveal the transition dipole moment at these wavelengths lies perpendicular to the molecular plane.

All these measurements suggest that the transition is induced by $b_1 \rightarrow a_1$ electron promotion in the C_{2v} symmetry. Electronic structure calculations predict that the excited states responsible for the transition are mainly the $^1B_1$ and $^1A_2$ states.[9-11] The $^1B_1$ state which has the Rydberg character is strongly bound and the valence $^1A_2$ state is repulsive along the asymmetric stretching vibrational coordinate that is correlated to HS+H. Among them, only the transition to the $^1B_1$ state is dipole allowed. Thus the dissociation mechanisms were proposed based upon those observations. The H_2S molecule is initially excited to the $^1B_1$ state that is bound along the symmetric stretching vibrational coordinate at the Franck-Condon region. The $^1B_1$ state is crossed by the repulsive $^1A_2$ state near the bottom of the $^1B_1$ potential energy surface forming a conical intersection. The $^1A_2$ state is repulsive along the asymmetric stretching vibrational coordinate and is correlated to the H + HS asymtote. Recent measurements of the emission spectra of H_2S excited at 199-203 nm clearly show an evidence of the conical intersection near 200 nm.[8] Upon excitation of H_2S near and above the conical intersection, the excited molecule initially feels the force along the symmetric stretching vibrational coordinate. As the dissociating molecule samples the conical intersection, an influence by the $^1A_2$ state leads the molecule to the exit channel repulsive along the asymmetric stretching vibrational coordinate. This description of dissociation dynamics is consistent with all of the previous observations except that the translational anisopropy is decreased as the photolysis wavelength is increased. Based upon the translational anisotropy measurement, another dissociation mechanism has been proposed. The initial excitation is to the $^1B_1$ state and the molecule is predissociated along the repulsive $^1A_2$ state. The reduction of translational anisotropy is explained by increase in lifetimes of the parent molecule at longer wavelengths due to the predissociation barrier.[3,10] However, this indirect dissociation mechanism fails to explain the smooth absorption in the longer wavelength side of the spectrum. In the adiabatic picture, the diabatic $^1B_1$ and $^1A_2$ states are correlated to the two $^1A''$ adiabatic surfaces along the asymmetric stretching vibrational coordinate in the C_s symmetry.[5] The $1^1A''$ state is purely repulsive and the $2^1A''$ state at higher energy is bound, both of which are all dipole allowed from the ground electronic state. The absorption is to both the repulsive $1^1A''$ state and the bound $2^1A''$ state leading to the structured absorption at the shorter wavelength side of the spectrum. However, at longer wavelength side of the continuum, a vertical transition from the ground state is expected to bring the molelcule directly to the repulsive part of the $1^1A''$ surface. In this case, the dissociation should be prompt and no reduction of the translational anisotropy is expected.

We performed the experiment to measure translational anisotropy of the fragment in the photodissociation of H_2S excited at 243 nm, *i.e.* longer wavelength side of the continuum. The experiment is simple and straightforward. We excited H_2S in a low pressure flow cell (150 mTorr) by irradiating focused 243 nm light (f=100 cm) produced by frequency-doubled output of an Nd:YAG pumped dye laser. The pulsewidth of the light is about 7 ns measured with a fast photodiode. The H_2S molecule absorbs a photon and is dissociated into H and HS and the fragment H atoms absorb subsequent two photons of the same wavelength within the same 7 ns pulse. The H atoms are then excited to the 2p state and the Lyman-α fluorescence is induced. The Lyman-α fluorescence has been detected with a solar blind photomultiplier tube (Hamamatsu R1259) whose direction of view is perpendicular to the propagation direction of the light. In order to reduce the scattered light and maximize the signal, we put a Lyman-α filter and flow dry nitrogen in the region between the exit window of the cell and the PMT. The polarization of the 243 nm light is horizontal, which is perpendicular to the propagation and thus the probe direction. The

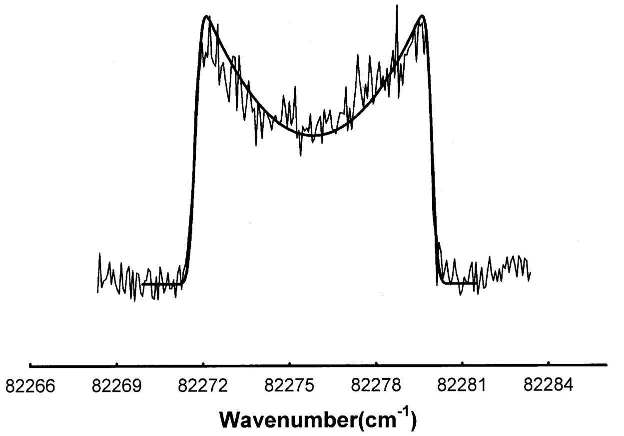

Figure 1. Observed H atom spectra produced from photodissociation of H_2S at 243 nm. The smooth curve is a fit by the equation given in the text with the anisotropy parameter β = -1 and the speed of the H atom being 14800 m/sec.

bandwidth of the laser light is 0.06 cm^{-1} measured by the linewidth of the gaseous I_2 spectra at ambient temperature.

The measured spectrum of H is presented in Figure 1. We measured the spectra at various laser powers. The log-log plot of the signal intensity vs. the laser power (1-3 mJ/pulse) shows a straight line with the slope of 3.20, confirming the three photon process. Thus one photon dissociation of H_2S and two photon absorption by the fragment H atoms can be estimated. The Doppler profile is fitted by the equation[12]

$$I(\nu) \propto 1 + \beta P_2(\cos\theta)$$

where β is the translational anisotropy parameter, P_2 is the second order Legendre polynomials, and θ is the angle between the transition dipole moment and the recoil direction of the fragment. The measured spectrum is successfully fitted by the above equation with β=-1 and the speed of H being 14,800 m/s. When a very short focal length lens is used (f=15 cm), the spot size is too small for us to fit the spectrum with β=-1 because the H atom moving perpendicular to the direction of the probe light is escaping out of the probing zone. The fact that the fraction of the available energy distributed to the translational energy of the fragment is 0.96 with little vibrational excitation of SH is in good agreement with the previous results. However, the measured anisotropy parameter is very different from the previous measurements. In the dissociation at long wavelengths (222, 248 nm) side of the absorption continuum, the previous measurements showed significant reduction of the anisotropy parameter from the limiting value, -1 for the pure perpendicular transition (-0.84 at 222 nm, -0.66 at 248 nm).[3,5] Previously, in order to measure the translational anisotropy, the fragment ion signal was measured by rotating a waveplate with respect to the detection axis in the TOF mass spectrometer. However, since the waveplate was cut for around 200 nm, the polarization might be smeared at 248 nm. In addition, the poor signal to noise at longer wavelengths compared to shorter wavelengths might prevent them from correct measurements of the anisotropy parameters.

In summary, the photodissociation of H_2S at 243 nm is prompt, at least the lifetime of the excited molecule is shorter than a rotational period. The two diabatic excited states, $^1B_1$ and $^1A_2$ are strongly coupled and are correlated to the adiabatic A'' surfaces along the asymmetric stretching vibrational coordinate. At 243 nm, longer wavelength side of the first continuum and energy below the conical intersection, the vertical transition from the ground state directly accesses the repulsive part of the $1^1A''$ adiabatic surface and the dissociation takes place along this potential surface.

Acknowledgment. This work has been financially supported by Korea Research Foundation and Korea Science and Engineering Foundation.

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