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193 nm photodissociation of H_2S: The SH internal energy distribution

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The dynamics of H_2S and D_2S photodissociation at 193 nm have been investigated using an ArF excimer laser to photolyze the parent compound and a tunable, doubled dye laser to probe the energy content of the SH or DH radicals via the laser induced fluorescence technique. The SH radicals are produced with nearly Boltzmann rotational distributions characterized by temperatures of 375 ± 15 and 220 ± 15°K for the $SH(^2\Pi_{3/2})$ and $SH(^2\Pi_{1/2})$ states, respectively. No vibrationally excited SH or SD fragments were observed. An upper limit on the $SH(v = 1)/SH(v = 0)$ ratio of 0.005 was determined. The ratio of $SH(^2\Pi_{3/2})$ to $SH(^2\Pi_{1/2})$ was 3.75 ± 0.20. Although roughly 20000 cm^{-1} of energy is available to the fragments, the average internal energy of the SH fragments is only 320 ± 20 cm^{-1}. Thus, most of the available energy must appear in the relative recoil coordinate between the H and SH fragments. This observation is in good agreement with the conclusions of previous studies and with a quasidiatomic kinematic picture of the dissociation.

I. INTRODUCTION

The importance of photodissociation to such diverse fields as reaction dynamics, atmospheric chemistry, and laser development has led historically to many experimental and theoretical attempts at measuring and interpreting the manner in which molecules fall apart. Modern experimental techniques can be traced to the introduction of flash photolysis by Norrish and Porter[1] and by Ramsay and Herzberg[2] during the 1950's. Flash photolysis made it possible for the first time to dissociate sufficient quantities of a parent molecule so that the internal energy content of transient photofragments could be observed by spectroscopic absorption. The modern application of this technique has led to two types of photofragment spectrometer. The first type, pioneered by Wilson and his collaborators[3] and now used routinely,[4-9] couples pulsed laser dissociation of molecules in a molecular beam with measurement of the fragment time of flight to a mass spectrometer. The recoil energy of the fragment is measured directly in this type of photofragment spectrometer, while the internal energy is inferred from the difference between the available energy and translational energies. In the second type of photofragment spectrometer, employed in the current study, the products of pulsed laser photolysis are detected using the technique of laser induced fluorescence.[10] The internal energy of the fragment is measured directly, while the translational energy is inferred from the difference between the available and internal energies. Many recent studies have shown that for favorable systems the laser induced fluorescence technique provides a simple method for obtaining the distribution of energy in the photofragments.[11-13]

Internal energy distributions of photofragments have also received considerable theoretical investigation using both semiclassical[14] and quantum mechanical[15-18] models. Perhaps the most extensive theoretical study of photofragment distributions has been performed by Morse, Freed, and Band, who have presented a generalized Franck–Condon theory for photodissociation.[19] In the more recent of their articles, methods have been developed to include a proper description of the initial bending modes for photodissociation of linear triatomic molecules. Such methods raise the hope that accurate predictions of photofragment internal energy distributions may soon be made for photodissociation of bent triatomic molecules.

The photochemistry of H_2S has been of interest to researchers since at least 1929.[20-31] The spectrum of this molecule between 190 and 230 nm is structureless with an absorption coefficient of roughly 0.23 $cm^{-1}\,Torr^{-1}$ at 193 nm.[22] While it is generally agreed that the primary dissociation is $H_2S \to H + SH$ in this region, the energy partitioning in the photofragments has not been systematically studied. Roughly 20000 cm^{-1} of energy is available to the fragments following dissociation at 193 nm. Porter[27] and Ramsay[28] have observed SH fragments in absorption following flash photolysis of H_2S, but only transitions from $v'' = 0$ of the $^2\Pi_i$ states to $v' = 0$ and $v' = 1$ of the $^2\Sigma^+$ state were detected. At the high pressures employed, however, it is likely that any vibrationally excited SH would have been collisionally relaxed before observation. The translational energy of the H atom has been measured indirectly by photolyzing varying mole fractions of H_2S in mixtures with perdeuterated reactants.[28-31] If the activation energies for $H + H_2S \to H_2 + SH$ and $H + RD \to HD + R$ are known, then the ratio of the HD to H_2 product provides an estimate of the translational energy of the H atom. At wavelengths of 253.7 nm,[30] 248 nm,[31] 228.8 nm,[29,30] 213.8 nm,[28,30] and 184.9 nm[30] it appears that greater than 50% of the available energy goes into the translational recoil of the H and SH fragments.

In this paper we report the investigation of H_2S and D_2S photodissociation at 193 nm using detection of SH or SD by laser induced fluorescence. The photofragment spectrometer is similar to those described previously.[11-13] In the regions near 323.7 and 306.0 nm the SH radical has strong $\tilde{A}\,^2\Sigma^+ \leftarrow \tilde{X}\,^2\Pi$ absorptions which have been analyzed by Lewis and White,[32] Porter,[26] and Ramsay.[27]

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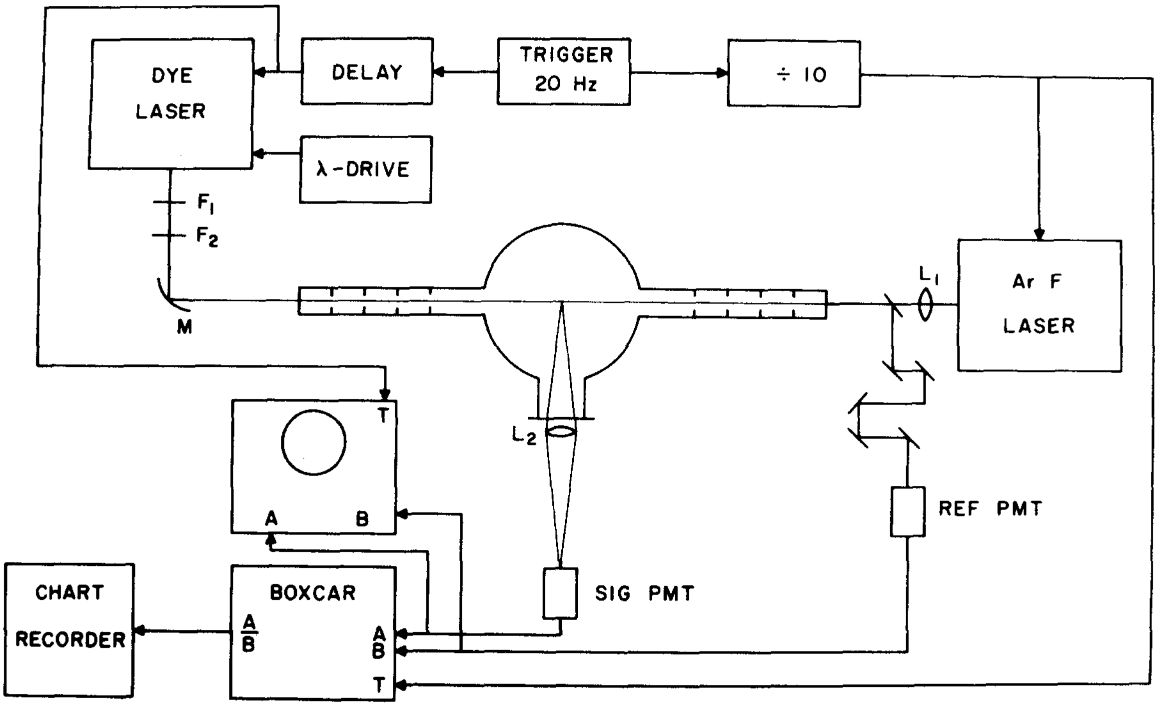

FIG. 1. Block diagram of the experimental apparatus. F_1 = Corning 7-54 filter. F_2 = Schott 305-nm cutoff filter. L_1 = 75-cm $f/1$ Suprasil lens. L_2 = 5-cm $f/1$ lens located 10 cm from laser beam and 10 cm from signal PMT. M = 2-m ROC aluminum mirror.

The lifetime of the $\tilde{A}$ state is 0.55 μsec.[33] The SH radical is therefore relatively easy to monitor in low concentrations by the laser induced fluorescence technique. From the previous studies of H_2S photodissociation[26–31] we would expect the SH fragment to have little internal energy. The results of our investigation show this to be the case.

II. EXPERIMENTAL

The experimental apparatus shown in Fig. 1 is of a design similar to that used by Baronavski and McDonald.[11] The apparatus consists of a photolysis laser, a tunable probe laser, a photolysis cell, and a photomultiplier tube with appropriate signal conditioning electronics.

The photolysis laser was a transverse discharge argon fluoride excimer laser which generated a pulse roughly 10 nsec long at 193.3 nm.[34,35] The measured linewidth was 1 nm FWHM and the frequency distribution was approximately Gaussian. The laser output power ranged from 15–30 mJ but was relatively stable over the time required to acquire a spectrum. The beam shape at the output mirror was roughly a 10×1 mm rectangle and was focused to a 3×0.5 mm rectangle by a 75-cm focal length Suprasil lens. The unfocused intensity was about 30 MW cm^{-2}, while the focused intensity exceeded 100 MW cm^{-2}. For a pulse energy of 25 mJ and an H_2S absorption coefficient of 0.23 $cm^{-1} Torr^{-1}$ at 193 nm,[22] it can be calculated that roughly 5×10^{15} photons will be absorbed by 10 mTorr of H_2S over the 80-cm pathlength of the photolysis cell if Beer's law is obeyed. Since there are only about 10^{15} molecules present in the laser beam at this pressure, it is clear that nearly all of the molecules in the beam will absorb a photon. It has been observed experimentally that fluctuations in the power of the photolysis laser seem to have little effect on the recorded spectrum, in agreement with the above calculation. Consequently, no attempt was made to correct the signal for variations in the power of the photolysis laser.

The probe laser was a tunable CMX-4 flashlamp pumped dye laser equipped with doubling crystals and an automatic wavelength scanner. Its spectral linewidth at visible wavelengths was about 3 cm^{-1}. This linewidth could be narrowed roughly an order of magnitude by the use of an intracavity etalon. For detection of SH, the laser was operated in its doubled and unnarrowed mode using Rhodamine 640. Two filters were placed near the output coupler of the dye laser. A Corning 7-54 filter was used to remove the residual fundamental, while a 305-nm cutoff filter was used to prevent the ArF laser from striking the dye laser. The latter filter passed the doubled dye laser pulse with little attenuation. The probe laser was mildly focused by a 2-m ROC aluminum mirror to a 1-mm diameter spot size in the center of the photolysis cell.

While continuous ultraviolet wavelength scanning of the probe laser was accomplished by the automatic scanning accessory, the angle of the doubling crystal had to be fine tuned manually from time to time during the course of a spectral scan. This adjustment was facilitated by splitting off part of the probe beam after it exited from the photolysis cell, reflecting this beam six times from quartz flats, and detecting the ultraviolet pulse with an Hamamatsu R212UH photomultiplier tube. The resulting signal was displayed on one channel of a dual-beam oscilloscope (Tektronix, model 556). The manual control on the automatic scanning accessory was then used to maintain the maximum ultraviolet output from the dye laser.

The dye laser pulse of about 1 μsec duration was delayed with respect to the ArF pulse. The shortest practical delay was determined by how effectively scattered light generated by the photolysis laser could be controlled. This scattered light was the result primarily of fluorescence from the Pyrex cell walls. A delay time of 1 μsec was a typical minimum. In order to trigger the dye laser during its resonant charging cycle, both the ArF and dye lasers were triggered by a source synchronized to the line frequency. The delay between the ArF and dye laser pulses was continuously adjustable to within a 200 nsec jitter.

The photolysis cell was constructed from a 5-liter (25-cm diameter) Pyrex round bottom flask. Two Pyrex tubes 30 cm long and 2.8 cm in diameter were attached to the flask on a line perpendicular to the neck and were used to pass the laser beams. Each tube was fitted externally with a Suprasil window and internally with four aluminum washers. The washers were coated with Aquadag and used to reduce the scattered light from the probe laser. Similar baffles have been used by Pruett and Zare.[36] Under typical operating conditions, the scattered light caused a 2-mV signal from the photomultiplier, while the laser induced fluorescence caused a 100-mV signal. The neck of the round bottom flask was retained as a viewing port and equipped with a Suprasil window attached with black wax. It allowed for collection of fluorescence reaching a 6-cm diameter circle located 20 cm from the photolysis region. A 25-cm focal length Suprasil lens was used to image about 0.4% of the fluorescence signal onto the cathode of an Hamamatsu R212UH photomultiplier tube. The entire cell was painted black on its external surface to exclude light not entering through the windows. It was then taped to prevent scratching.

The signal conditioning electronics consisted of a dual channel boxcar averager (PAR 162/164/164), an oscilloscope, and a chart recorder. The gate of the boxcar was synchronized to the dye laser pulse. The fluorescence signal from one photomultiplier tube was input to the *A* channel of the boxcar, while the dye laser reference signal from the second photomultiplier tube was input to the *B* channel. The ratio feature of the averager was used to provide an *A*/*B* output signal which automatically compensated for any variation of dye laser power with wavelength. Because the two photomultiplier tubes had the same wavelength response and because the fluorescence from the SH fragment occurs primarily at the excitation wavelength, this system had the further advantage that it corrected for almost all of the variation in the spectral response of the photomultiplier tube. A typical spectrum was recorded with a scan rate of 0.05 cm^{-1} per ArF laser pulse and with a signal-to-noise enhancement ratio of about 5.

H_2S was obtained from Matheson at a stated purity of 99.5%, while D_2S was obtained from Merck at an isotopic purity of 98%. Both gases were used without further purification. Cell pressures were measured with a capacitance manometer (MKS, Type 310 BHS-1) accurate to 2% at 10^{-4} Torr. The cell was connected to a greaseless vacuum line which could evacuate the cell to pressures below 10^{-6} Torr. When switching between H_2S and D_2S the vacuum line and cell were thoroughly passivated with the new gas.

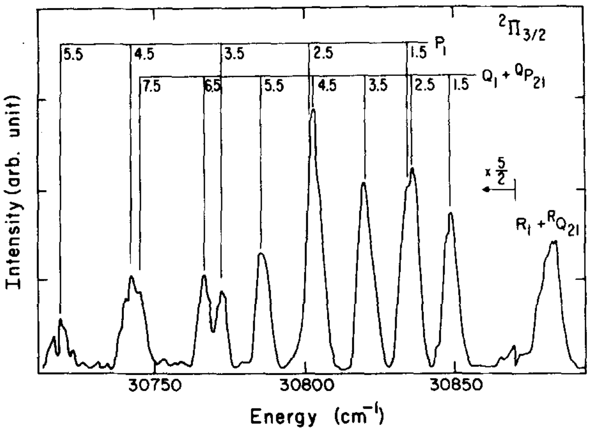

FIG. 2. Portion of the SH laser induced fluorescence spectrum recorded for an initial H_2S pressure of 5 mTorr and a delay time of 1.0 μsec between the photolysis and probe laser pulses. The assignments are the rotational transitions in the ($v'=0 \leftarrow v''=0$) band of the $^2\Sigma^+ \leftarrow {}^2\Pi_{3/2}$ system. The signal intensities to the left of the arrow have been expanded by a factor of 5/2.

III. RESULTS

A. Rotational distribution

Figure 2 displays the SH laser induced fluorescence spectrum recorded near 30 800 cm^{-1} for an initial H_2S pressure of 5 mTorr and a delay time of 1.0 μsec between the photolysis and probe lasers. Spectra with slightly different intensity distributions were obtained for 40 mTorr and 2.5 μsec and for 10 mTorr and 1.0 μsec. The assignments of Fig. 2 identify the rotational transitions in the ($v'=0 \leftarrow v''=0$) band of the $^2\Sigma^+ - {}^2\Pi_{3/2}$ system and are based on the work of Lewis and White,[32] Ramsay,[27] and Porter.[26] A similar spectrum was obtained for the $^2\Sigma^+ \leftarrow {}^2\Pi_{1/2}$ system.

The Λ components of each rotational doublet were found to be equally populated. The $R_1 + {}^RQ_{21}$ and the P_1 branches probe absorption from the positive Λ component in the $^2\Pi_{3/2}$ state, while the $Q_1 + {}^QP_{21}$ branch probes absorption from the negative Λ component. The integrated populations determined from these branches were equal to within 5%.

B. Vibrational distribution

Several attempts were made to observe any SH($^2\Pi_i$, $v''=1$) produced by the dissociation. The ($v'=1 \leftarrow v''=1$) transitions from SH($^2\Pi_{3/2}$) and SH($^2\Pi_{1/2}$) to SH($^2\Sigma^+$) lie near 30 105 and 29 725 cm^{-1}, respectively, but no laser induced fluorescence was observed when scanning through these regions. This result is not surprising, since the SH($^2\Sigma^+$, $v'=1$) level is known to be predissociated by the nearby crossing of a $^2\Sigma^-$ curve.[27] Three methods for overcoming this spectroscopic difficulty were used.

Attempts were made to observe the DS($v''=1$) product from D_2S photolysis. D_2S is similar in its photodissociation to H_2S.[26,27] However, the $SD(^2\Sigma^+, v'=1)$ level lies below the corresponding level in SH and is not appreciably predissociated.[27] A search for SD laser induced fluorescence on the $(v'=1 \leftarrow v''=1)$ band failed to yield observable signals. Unfortunately, the sensitivity of this experiment was limited by trace amounts of H-atom impurities which resulted in a weak $SH(^2\Sigma^+ \leftarrow {}^2\Pi_{1/2}, v'=0 \leftarrow v''=0)$ spectrum in the region where the $SD(v'=1 \leftarrow v''=1)$ band was expected. The upper limit on the $DS(v''=1)/DS(v''=0)$ ratio was determined to be 0.005. In order to verify that $DS(v''=1)$ could have been detected if present, this species was monitored following its creation in the $F + D_2S$ reaction. The experimental system for initiating this reaction was similar to that described elsewhere,[37] while the apparatus used for detection of SD was identical to that used here. Appreciable $DS(v=1)$ signals from the $F + D_2S$ reaction were observed, while none were observed following direct photolysis of D_2S. This result lends further support to the conclusion that the DS product of D_2S photolysis has very little vibrational excitation.

Attempts were also made to relax any vibrationally excited SH and to measure the resulting difference in the $SH(v''=0)$ excitation spectrum intensity. The excitation spectrum was recorded with and without 100 Torr of N_2 added to 20 mTorr of H_2S. In order to minimize the diffusion of SH out of the probe beam in the absence of N_2, the shortest possible delay was used between the photolysis and probe pulses. The difference in total integrated intensity between the two spectra was less than 2%. N_2 might reasonably be expected to relax SH since its vibrational frequency $(\omega_e = 2360\ \text{cm}^{-1})$ is close to that for $SH(\omega_e = 2700\ \text{cm}^{-1})$. The absence of an appreciable difference between the two spectra indicates that the $SH(v''=1)/SH(v''=0)$ ratio is probably less than 0.02.

Finally, an attempt was also made to probe the $SH(^2\Sigma^+ \leftarrow {}^2\Pi_i, v'=0 \leftarrow v''=1)$ transition. The Franck–Condon factor for this transition was not known prior to our experiments, so that the absence of any observed signal did not provide a limit on the $SH(v''=1)/SH(v''=0)$ ratio. We have subsequently measured the Franck–Condon factor by exciting the SH product of the $F + H_2S$ reaction on its $(v'=0 \leftarrow v''=0)$ $R_1 + {}^RQ_{21}$ bandhead transition and resolving the fluorescence with a monochromator (Spex 1702). The resulting fluorescence spectrum is shown in Fig. 3, which identifies the transitions from $v'=0$ of the $^2\Sigma^+$ state to $v''=1$ and $v''=0$ of the $^2\Pi_i$ states. The observation that the $(v'=0 \rightarrow v''=1)$ transition is only 0.059 times the intensity of the $(v'=0 \rightarrow v''=0)$ transition allows us to place an upper limit of 0.005 on the $SH(v''=1)/SH(v''=0)$ ratio.

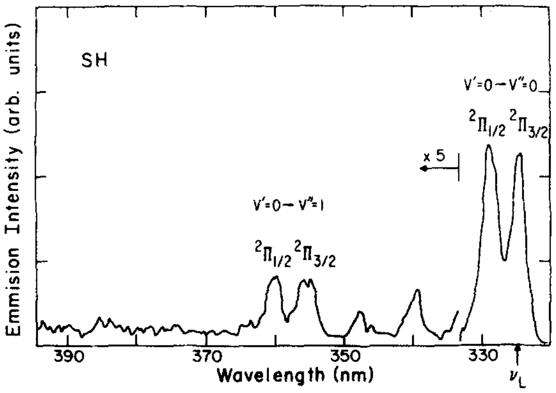

FIG. 3. Fluorescence spectrum produced by exciting SH on its $(v'=0 \leftarrow v''=0)$ $R_1 + {}^RQ_{21}$ band head. Fluorescence is observed from $v'=0$ of the $^2\Sigma^+$ state to $v''=0$ and 1 of each of the $^2\Pi_i$ states. The signal intensities to the left of the arrow have been expanded by a factor of 5.

C. Electronic distribution

The laser induced fluorescence spectra of the $^2\Sigma^+ \leftarrow {}^2\Pi_{3/2}$ and $^2\Sigma^+ \leftarrow {}^2\Pi_{1/2}$ systems were compared under identical conditions of starting pressure (5 mTorr), delay time (1 μsec), and detection geometry. The integrated intensity of the $^2\Pi_{3/2}$ system was found to be 3.75 ± 0.20 times that of the $^2\Pi_{1/2}$ system.

IV. DISCUSSION: THE ENERGY DISTRIBUTION OF THE SH FRAGMENT

The preceding results have shown that the SH product of 193-nm dissociation of H_2S is born with very little internal excitation. The $^2\Pi_{3/2}/{}^2\Pi_{1/2}$ ratio of 3.75 corresponds to an electronic temperature of 410 °K. The upper limit on the fraction of vibrationally excited SH in either electronic state was found to be $SH(v''=1)/SH(v''=0) \leq 0.005$. This ratio corresponds to a maximum vibrational temperature of 700 °K. The rotational distribution was also found to be unexcited. Formulas for the line strengths of various rotational branches have been given by Earls for the general case of a $^2\Sigma \leftarrow {}^2\Pi$ transition with arbitrary spin–orbit splitting.[38] Dieke and Crosswhite have presented a detailed method for converting spectroscopic intensities to relative rotational populations once the line strengths are known.[39] The intensities of the rotational lines in Fig. 2 for the $^2\Pi_{3/2}$ state were converted to relative rotational populations using the methods described in these two references. The logarithm of the resulting populations is plotted as a function of rotational energy in Fig. 4, where the straight line is the fit to the data of a Boltzmann distribution with a temperature of 375 °K. A similar analysis for the $^2\Pi_{1/2}$ state yielded the distribution of Fig. 5. The fit is to a Boltzmann distribution at 220 °K. It is likely that the measured rotational distributions are unrelaxed. Only 0.05 hard sphere collisions $(\sigma = 46\ \text{Å}^2)$ occur at 5 mTorr during the 1 μsec delay between the photolysis and probe pulses used in the experiment. Furthermore, the $^2\Pi_{3/2}$ spectra taken at 40 mTorr and 2.5 μsec and at 10 mTorr and 1.0 μsec give rotational temperatures of 305 and 360 °K, respectively. While the effect of rotational relaxation is noticeable in these high pressure spectra, the relaxation rate is not large enough to have an appreciable effect on the spectrum taken at 5 mTorr and 1 μsec. We conclude that little of the 20 000 cm^{-1} in available energy appears in the SH rotational, vibrational, or electronic degrees of freedom. By inference, most of the available energy must appear in the relative recoil coordinate between the H and SH fragments.

Our conclusion that most of the available energy is channeled into the recoil velocity is in good agreement with the results of relative reactivity studies.[28-31] At a dissociation wavelength of 213.8 nm Gann and Dubrin[28] and Sturm and White[30] estimated that 100% or 80%, respectively, of the available energy appears as kinetic energy of separation. At 184.9 nm, the latter authors found that 57% of the available energy appears in the recoil coordinate. From a weighted average of the $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ internal energies, we calculate from our results at 193 nm that the SH fragment has 320 ± 20 cm^{-1} of internal energy. Since the available energy is ~20 000 cm^{-1}, the fraction of energy which appears as translational recoil is 98%. Sturm and White have noted an apparent decrease from 96% to 57% in the fraction of energy appearing as translational recoil as the dissociation wavelength decreased from 257.3 to 184.9 nm.[30] Our single results at 193 nm suggests that the decrease might not be so dramatic, although more work at other wavelengths will be needed to settle this question.

The results of our investigation are also in good agreement with the predictions of a simple quasidiatomic kinematic model for the dissociation. The major assumptions of this model have been reviewed elsewhere.[14] While detailed calculations for the H_2S case have not been performed, the basic features of the kinematics follow easily from the assumption that the dissociation takes place along the original H–SH bond. Since the HSH bond angle is 92°, it is clear that recoil along the original bond is nearly orthogonal to the SH vibrational mode. It is not likely therefore, that the recoil will couple energy into product vibration.[31] Furthermore, the SH bond distance in H_2S(1.328 Å) is nearly the same as that in SH(1.340 Å). Consequently, a simple Franck–Condon picture of the dissociation[17,19] would also predict that the SH is formed primarily in $v = 0$. The absence of SH rotational excitation also follows from the assumption that the dissociation takes place along the original H–SH bond. By conservation of angular momentum, the initial rotation of the H_2S (J) must be partitioned into the internal angular momentum of the SH fragment (J′) and the orbital angular momentum (L′) of the half-collision on the repulsive surface: $\mathbf{J} = \mathbf{J}' + \mathbf{L}'$. The maximum value of L' is equal to $\mu v_{\max} b$, where $\mu \simeq 1$ amu is the H–SH reduced mass, $v_{\max} \simeq 2 \times 10^6$ cm/sec is the maximum relative recoil velocity, and b is the impact parameter for the half-collision. If dissociation takes place along the original H–SH bond, then $b = 4 \times 10^{-2}$ Å and $L'_{\max} \simeq 1.3\hbar$. By contrast, the average values of J and J' are much higher. For example, $J' \simeq 5\hbar$ from the measured distribution for the $^2\Pi_{3/2}$ state (Fig. 4). If we make the approximation that $L' \ll J, J'$, then $J \simeq J'$, or the rotational momentum of the SH fragment is simply equal to the original rotational momentum of the H_2S parent. The energy corresponding to the angular momentum of the SH fragment (320 ± 20 cm^{-1}) is indeed close to the original rotational energy of the H_2S parent ($\frac{3}{2}RT = 315$ cm^{-1}). The observation that the Λ components of the rotational levels are equally populated is also consistent with the quasidiatomic picture of the dissociation. This picture predicts that L' is so small that the SH rotation is almost entirely derived from the original H_2S rotation. If the rotation were derived from the recoil of dissociation, then we would expect the rotational angular momentum to be perpendicular to the singly occupied Π orbital; only the Π^+ component would be populated. Since both components are equally populated, L' must be small, in agreement with the quasidiatomic picture of the dissociation. We conclude that all of our observations concerning the energy distribution in the SH fragment are consistent with this simple quasidiatomic picture of the dissociation.

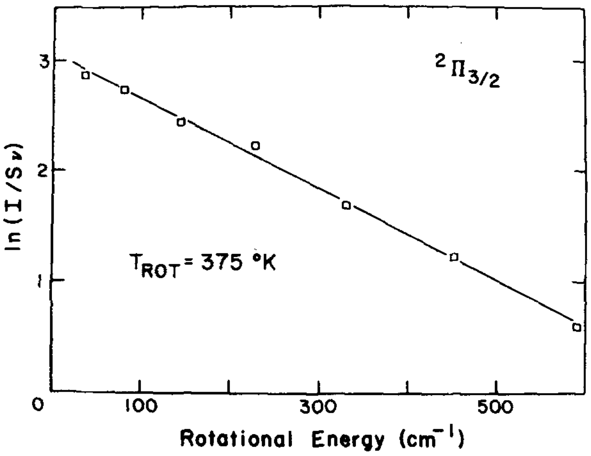

FIG. 4. Relative rotational populations of the $^2\Pi_{3/2}$ ($v'' = 0$) level as a function of rotational energy. The solid line is a fit of the data to a Boltzmann distribution with a temperature of 375 °K.

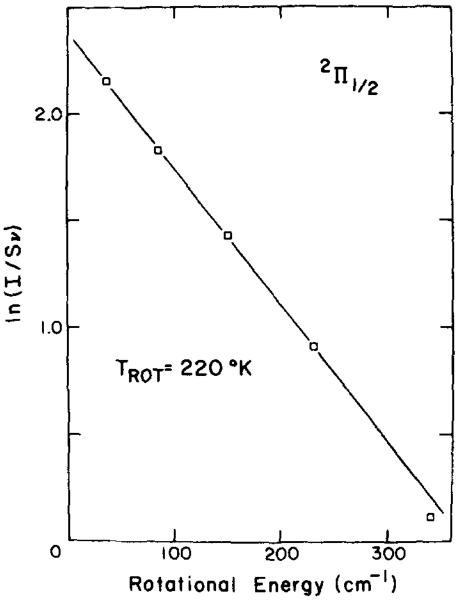

FIG. 5. Relative rotational populations of the $^2\Pi_{1/2}$ ($v' = 0$) level as a function of rotational energy. The solid line is a fit of the data to a Boltzmann distribution with a temperature of 220 °K.

V. CONCLUSION

Of the 20 000 cm^{-1} in energy which is available to the H + SH fragments following 193-nm dissociation of H_2S, only 320 ± 20 cm^{-1} appears in the internal coordinates of the SH. This observation is consistent with a simple kinematic model in which the H atom departs from the SH fragment along the direction of its original bond. Since the measured internal energy of the SH fragment is small and nearly equal to the original internal energy of the H_2S parent, it will be difficult to measure the variation in SH internal energy with dissociation wavelength. One method for making such a measurement might be to cool the H_2S rotationally by expansion in a supersonic nozzle beam. Experiments of this type are currently in progress in our laboratory.

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