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Photofragment spectroscopy of CS₂ at 193 nm: Direct resolution of singlet and triplet channels

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The 193 nm dissociation of CS₂ has been studied under supersonic molecular beam conditions, with the atomic S products detected by vacuum ultraviolet laser-induced fluorescence. These experiments measure the branching ratio between singlet and triplet channels to be $S({}^{3}P)/S({}^{1}D) = 2.8 \pm 0.3$. Doppler spectroscopy on the $S({}^{3}P_{2})$ and $S({}^{1}D_{2})$ products was used to study the dynamics of each channel separately. The energy release in each channel was similar, with the CS fragments formed vibrationally inverted with about 50% of the available energy in CS rotation and vibration. The recoil velocity anisotropy in each channel was also measured, found to be the same for both, and was consistent with a 2 ps lifetime for the ${}^{1}\Sigma_{\mu}^{+}({}^{1}B_{2})$ excited state of CS₂.

INTRODUCTION

Progress in our understanding of photofragmentation dynamics has resulted from the very detailed study of the photofragment spectroscopy of a relatively small number of molecules,¹ in particular triatomic molecules.² One very important class of triatomics that has received a great deal of attention, both theoretical and experimental, are a series of 16 valence electron linear triatomics (e.g., CO₂, OCS, ICN, N₂O, and CS₂).³ The photochemistry of CS₂ has been studied by several different groups in recent years, with attention being focused on the 193 nm photolysis using an ArF excimer laser. The ArF laser output matches a band in the ${}^{1}\Sigma_{u}^{+}({}^{1}B_{2}) \leftarrow X{}^{1}\Sigma_{g}^{+}$ absorption system, the strongest feature in the CS₂ absorption spectrum with an oscillator strength $f = 1.1.^{3}$

At first glance, the absorption system is quite simple, a progression of bands $\approx 410 \text{ cm}^{-1}$ apart in a broad envelope from 46 000 to 53 000 cm⁻¹, peaking around 50 000 cm⁻¹. At high resolution however, this spectrum is very complex⁴ and has thus far defied detailed analysis. It has been determined that there is a large geometry change upon excitation to the ${}^{1}\Sigma_{\mu}^{+}({}^{1}B_{2})$ state, with the S-C-S bond angle decreasing from 180° in the $X^{1}\Sigma_{g}^{+}$ state to 153° in the $\Sigma_{u}^{+}({}^{1}B_{2})$ state, and the C-S bond distance lengthening from 1.55 to 1.66 Å.⁴ This results in excitation of both the symmetric stretching vibration and the bending vibration in the excited state. These two vibrations, which are close in energy in the ground state (658 and 396 cm^{-1}) and have the same symmetry in the $C_{2\nu}$ excited state, should be strongly mixed in the ${}^{1}\Sigma_{\mu}^{+}({}^{1}B_{2})$ state, leading to the complex structure in the absorption spectrum. A more recent study has determined that for excitation of low energy bands (below $50\ 000\ cm^{-1}$) the radiative lifetime of the ${}^{1}\Sigma_{u}^{+}$ (${}^{1}B_{2}$) state varies from 9 to 1 ps, declining sharply with increasing energy.⁵ In a pulsed jet experiment on supersonically cooled CS₂, Hemley et al.⁶ showed that the general features of the spectrum were well described by two coupled modes, v_1' and v_2' , with frequencies of 392 and 426 cm⁻¹. The linewidth in the jet ($T_{\rm rot} \approx 10$ K) for the band excited by the ArF laser is on the order of 20 cm⁻¹, implying a dissociation lifetime on the order of 0.3 ps or longer. This band, which has more than one vibrational component, corresponds to at least 13 quanta in the v'_1 and v'_2 modes, and thus excitation of CS₂ with an ArF laser results in a ¹B₂ state with significant excitation in both stretching and bending coordinates. Further, the analysis of Hemley *et al.*⁶ would indicate that this excitation energy is above the barrier to linearity in the excited ${}^{1}\Sigma_{u}^{+}({}^{1}B_{2})$ state, and thus excitation of CS₂ at 193 nm results in a quasilinear CS₂ molecule.

It is generally agreed that the fate of the ${}^{1}\Sigma_{u}^{+}({}^{1}B_{2})$ excited state is predissociation into CS and S:

$$CS_2 + hv \rightarrow CS_2^*({}^{1}B_2) \rightarrow CS({}^{1}\Sigma^+) + S({}^{1}D)$$
(1a)

$$\rightarrow \mathrm{CS}(^{1}\Sigma^{+}) + \mathrm{S}(^{3}P). \qquad (1b)$$

The only energetically allowed channels at 193 nm are given above, with the excess energy for 193 nm excitation being 18.6 kcal/mol for reaction (1a) and 45 kcal/mol for reaction (1b).⁷ Beyond this, however, there is little agreement in the literature about the photochemistry of the ${}^{1}B_{2}$ state of CS₂. In an early flash photolysis study by Callear,⁸ CS_2/N_2 mixtures were photolyzed with light in the 190–210 nm range, and the transient absorption of the vibrationally excited CS and $S(^{3}P)$ products were observed. His conclusions were that the major photolysis reaction was reaction (1b) and that 75% of the CS products were formed with v'' > 2. Shortly after, a chemical trapping study by deSorgo et $al.^9$ found that photolysis of CS₂ in the 195–225 nm range resulted in a $S(^{3}P)$ product, with no evidence being found for the $S(^{1}D)$ product, again indicating that the primary photochemistry is essentially reaction (1b). Both of these early studies were carried out at high pressure, where one would expect a rapid quenching of any $S(^{1}D)$ product to $S(^{3}P)$, and thus the fact that these studies did not find evidence for reaction (1a) is not surprising.

A series of experiments carried out over the last eight years on the collision-free photochemistry of CS_2 have led to contradictory conclusions about the relative importance of

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reactions (1a) and (1b). In the earliest of these, a study by Yang et al.,¹⁰ molecular beam photofragment translational spectroscopy and laser-induced fluorescence (LIF) detection of CS were used to determine the energy release in the photofragmentation, and the relative importance of reactions (1a) and (1b). The authors interpreted their data as indicating that the major reaction channel was reaction (1a), the spin allowed dissociation, with the relative yield of $S(^{3}P)/S(^{1}D)$ being 0.25 \pm 0.15. This was contradicted very shortly after by a study carried out by Addison et al.,¹¹ in which $S(^{1}D)$ was detected by resonance fluorescence using an atomic lamp. Their results were interpreted as showing that $S(^{1}D)$ was a minor product, with the branching ratio being $S(^{3}P)/S(^{1}D) \approx 6$. In a paper on excited state CS formed by multiple photon dissociation of CS₂, Dornhofer et al.¹² suggested that the cause of this discrepancy was dissociation of the CS photoproduct by the ArF laser, and then concluded that if this was the case, the true branching ratio was $S(^{3}P)/S(^{1}D) = 3$. In a study similar to Yang et al., McCrary et al.¹³ looked at the photofragment time of flight and detected the CS photoproduct by LIF and concluded that the branching ratio was $S(^{3}P)/S(^{1}D) = 0.66$.

In a recent paper, Black and Jusinski¹⁴ reported experiments in which the $S({}^{3}P_{2})$ photoproduct was detected by multiphoton ionization, from which they concluded the branching ratio to be $S({}^{3}P)/S({}^{1}D) = 5.7 \pm 2$.

Finally, Kanamori and Hirota²⁶ used transient infrared absorption spectroscopy to detect the CS photoproduct resulting from 193 nm photolysis of CS_2 in a gas cell. By an analysis of the Doppler line shapes for various CS(v,J) absorption lines, the authors concluded that the $S({}^{3}P)/S({}^{1}D)$ ratio was approximately one.

Although not completely in agreement, there is a bit more of a consensus on the energy release in the CS₂ photodissociation. Both photofragment translational spectroscopy^{10,13} and laser-induced fluorescence^{10,13,15} indicate that the CS is formed vibrationally excited in an inverted distribution, peaking around v'' = 3. The details of the distribution vary between studies, and none of the studies can provide a definitive separation of CS(v'') product into the two possible reaction channels. The picture of CS₂ photofragmentation thus remains quite murky, in spite of extensive work.

In this paper, we provide for the first time an unambiguous description of the photofragmentation dynamics of CS_2 . The method we have chosen is different from those used previously, and directly resolves the two possible reactions under strictly collision-free conditions. In these experiments, we have used coherent vacuum ultraviolet¹⁶ to detect the atomic sulfur products of 193 nm photolysis of CS₂, using laser-induced fluorescence LIF as the detection method. This detection method is exceedingly sensitive, particularly for atomic products, and thus provides the immediate advantage that all experiments were carried out under low density molecular beam conditions, using very low fluences of photolysis laser light. The well defined linear spectroscopic detection method which was used allowed direct measurement of the nascent relative yields of $S(^{3}P)$ and $S(^{1}D)$, with no reliance on collisional relaxation. Finally, the high resolution of the VUV probe laser (resolving power of 350 000) enabled us to use Doppler spectroscopy to probe S atom products, leading to direct resolution of the dynamics of reactions (1a) and (1b). The use of Doppler spectroscopy in conjunction with a polarized photolysis laser allowed both the translational energy distribution and photofragment velocity anisotropy to be measured for both channels.

EXPERIMENTAL

The experimental method used has been described in previous publications.^{17,18} Briefly, a pulsed supersonic jet of 1% or 5% CS_2 in helium is crossed by the ArF photolysis laser (Questek 2200). The CS₂ (Baker) was put into a glass reservoir and degassed by repeated freeze/pump/thaw cycles. The reservoir was connected to the gas inlet system for the beam source and held at constant temperature (-23 or -46 °C) by a slush bath. The helium carrier gas flowed through the CS₂ reservoir, and the resulting gas mixture (total pressure 900 Torr) was expanded out of the source. A short time delay later, typically 1 μ s, the probe laser was sent through the photolysis volume, and the atomic S products were detected by VUV LIF. The probe laser used was tunable coherent VUV generated by resonant four-wave sum mixing in Mg vapor¹⁶ and was tunable over the 140-170 nm spectral range.¹⁹ The S atom products were detected by excitation of the ${}^{1}P_{1}^{\circ} \leftarrow {}^{1}D_{0}$ line at 1448.23 Å and the lines in the ${}^{3}D_{J'} \leftarrow {}^{3}P_{J''}$ multiplet in the 1474.0 to 1483.2 Å region. For the relative yield and photolysis power dependence experiments, the ArF laser beam was unpolarized. The laser was run in constant pulse energy mode, attenuated by layers of stainless steel mesh, telescoped down in size, and spacially filtered by an iris before it entered the molecular beam apparatus. The pulse energies used were in the 100 to 1000 μ J/ pulse range, with the spot being approximately 2 by 5 mm. In order to record the Doppler spectra, the photolysis laser was polarized by a stacked plate polarizer consisting of 12 fused silica plates at Brewster's angle. The linewidth of the probe laser was measured by recording the fluorescence excitation spectrum of CO in the pulsed supersonic jet, and using an isolated line in the $A^{1}\Pi \leftarrow X^{1}\Sigma^{+}(3,0)$ band to determine the line shape.

In order to check for linearity in the detection system, the VUV probe laser power was varied by attenuating the dye laser beams with neutral density filters and monitoring both the VUV laser intensity and the S atom LIF signal. In all experiments both the LIF signal and VUV intensity were recorded simultaneously. The excimer laser power was measured by a Gentec ED200 energy meter, and was monitored throughout the experiments.

RESULTS AND ANALYSIS

$S(^{3}P)/S(^{1}D)$ branching ratio, $S(^{3}P_{J})$ distribution

It has been suggested previously that secondary photolysis of the CS photoproduct could distort the relative yields of products,¹² so the effect of ArF laser power on product yield was investigated. The yield of $S({}^{3}P_{2})$ and $S({}^{1}D_{2})$ was measured as a function of laser power for pulse energies between 100 and 1000 μ J/pulse. Under our focusing condi-

tions for the excimer laser, this corresponded to energy fluences of between 1 and 10 mJ/cm², and power fluences of between 0.07 and 0.7 MW/cm². Although power densities were not always specified, it would appear that the highest power density used in this study was about 2-4 times lower than used in previous studies^{13,15} and about 100 times lower than that used by Dornhofer et al.¹² The results of these experiments are shown in Fig. 1 and as can be seen, the product yield is proportional to laser power, with no nonlinearity over the power range studied. In order to ensure there was no distortion of the $S(^{3}P)/S(^{1}D)$ yield, all work reported here was carried out with an ArF energy fluence of 1 mJ/cm². The VUV probe laser is narrow band and quite intense, so we also verified that the atomic transitions were not saturated by observing how the LIF signal varied with VUV probe power. In all cases, a strictly linear power dependence was observed, and the branching ratio measured was independent of VUV laser power.

In order to measure the $S({}^{3}P)/S({}^{1}D)$ branching ratio, the various product S resonance lines were recorded and the signals integrated. In all cases, the laser linewidth was less than the product Doppler width. Experiments were carried out with beams of 1% CS₂ in He and 5% CS₂ in He, and the results were the same for both CS₂ concentrations, indicating that the effect of clusters on the observed branching ratio was insignificant.

For comparison between the $S({}^{3}P)$ product and the $S({}^{1}D)$ product intensities, the ${}^{3}D_{3}^{\circ} \leftarrow {}^{3}P_{2}$ lines at 1474.01 Å and the ${}^{1}P_{1}^{\circ} \leftarrow {}^{1}D_{2}$ line at 1448.25 Å were recorded at several different excimer powers and VUV probe laser powers for the 1% CS₂ and 5% CS₂ beams. The ratio of the integrated LIF signal divided by VUV laser power was found to be $I({}^{3}P_{2})/I({}^{1}D_{2}) = 1.31 \pm 0.12$, where $I({}^{3}P_{2})$ is the integrated signal for the ${}^{3}D_{3}^{\circ} \leftarrow {}^{3}P_{2}$ line divided by laser power and $I({}^{1}D_{2})$ is the corresponding signal for the ${}^{1}P_{1}^{\circ} \leftarrow {}^{1}D_{2}$ line. The detecting photomultiplier was a solarblind tube with a CsI photocathode (EMR 542G-08-17). The observed signal



FIG. 1. Observed S atom laser-induced fluorescence signal as a function of 193 nm photolysis laser power. Signals for the ${}^{1}P_{1} - {}^{1}D_{2}$ (squares) and ${}^{3}D_{3} - {}^{3}P_{2}$ (circles) resonance lines are shown, with all signals being divided by the VUV laser power.

ratio was corrected for the relative detectivity of the LIF system for $S({}^{3}P_{2})$ and $S({}^{1}D_{2})$ by using the manufacturer's response calibration for the phototube. As the light collection optics were all uncoated LiF, there was no correction necessary for their transmission. The upper state for the ${}^{3}D_{3}^{\circ} \leftarrow {}^{3}P_{2}$ line only radiates back to the ${}^{3}P_{2}$ state, and thus all of the fluorescence excited was at 1474 Å, while for the ${}^{1}P_{1}^{\circ} \leftarrow {}^{1}D_{2}$ transition, the ${}^{1}P_{1}^{\circ}$ state radiates at 1448 Å (${}^{1}P_{1}^{\circ} - {}^{1}D_{2}$) and at 1782 Å (${}^{1}P_{1}^{\circ} - {}^{1}S_{0}$). The branching ratio for the ${}^{1}P_{1}^{\circ}$ fluorescence is known²⁰ and is 82% at 1448 Å and 18% at 1782 Å. The quantum efficiency of the detector tube was 11% at 1448 and 1474 Å and 2.5% at 1780 Å, meaning that a correction factor of $1/(0.82 + 0.18 \times 2.5/$ 11) = 1.16 was used for the $I({}^{1}D_{2})$, resulting in a detector corrected intensity ratio of $I({}^{3}P_{2})/I({}^{1}D_{2}) = 1.13 \pm 0.10$.

In order to interpret these relative intensities, values of the line strengths for the S atomic lines are needed. Unfortunately, these line strengths are somewhat uncertain, and this is the major source of error in our determination of the $S(^{3}P)/S(^{1}D)$ branching ratio. The literature values for the degeneracy corrected oscillator strengths are²⁰ (gf) = 0.37 for the ${}^{3}D_{3}^{\circ} - {}^{3}P_{2}$ line and (gf) = 0.65 for the ${}^{1}P_{1}^{\circ} - {}^{1}D_{2}$ line. The absolute value of these oscillator strengths are accurate to 50%, but the ratio is probably more accurate, as both were determined by the same technique. Separate calibration experiments²¹ have not yet yielded a more accurate value of the line strength ratio. A preliminary measurement of the ratio of line strengths found a value $gf({}^{1}P_{1}^{\circ} - {}^{1}D_{2})/gf({}^{3}D_{3} - {}^{3}D_{2}) = 1.0^{28}$ (vs a literature value of 1.7), but subsequent measurements have found this ratio to be too low. Using the literature values for the line strengths, we get a product population ratio of $S({}^{3}P_{2})/$ $S(^{1}D) = 1.96 \pm 0.17$, where the uncertainty quoted does not include the uncertainty in the line strengths.

In order to determine the overall ${}^{3}P/{}^{1}D$ branching ratio, the distribution of S(${}^{3}P_{J}$) product must be known. This was accomplished by monitoring the intensities of the ${}^{3}D_{2}^{\circ} \leftarrow {}^{3}P_{1}$ and $D_{1}^{\circ} \leftarrow {}^{3}P_{0}$ lines at 1483.04 and 1487.15 Å. The relative line strengths within the multiplet are well known^{20,22} and the relative populations that we have determined are ${}^{3}P_{2}$: ${}^{3}P_{1}$: ${}^{3}P_{0} = 0.71$:0.25:0.04. This spin-orbit distribution can be described by a temperature of 700 K. This distribution also indicates that the S(${}^{3}P_{2}$) is 71% of the total S(${}^{3}P_{J}$) product, and thus the overall S(${}^{3}P)/S({}^{1}D$) branching ratio is 2.78 \pm 0.25.

Doppler spectroscopy

It has been known for some time that the fixed orientation of the transition dipole in a molecule can give rise to an anisotropic distribution of photofragments.^{23,24} Photolysis with a polarized laser preferentially excites molecules with the transition dipoles aligned with the laser polarization. As long as the dissociation lifetime is shorter than the rotation time of the molecule, this will result in a preferential product recoil direction with respect to the photolysis laser polarization, resulting in an anisotropic distribution of photofragments. In general, the photofragment angular distribution is given by²⁵

$$I(\theta) = (4\pi)^{-1} [1 + \beta P_2(\cos \theta)],$$
 (2)

where θ is the angle between the recoil velocity v, and the laser polarization E, and β is the anisotropy parameter $(-1 \le \beta \le 2)$. This anisotropy is reflected in the Doppler profile for photofragment emission or absorption along a given axis.²⁴ The Doppler shift Δv_D for a given product velocity v₀ is proportional to the projection of the velocity onto the probe laser axis k, with $\Delta v_D = v_0(|v_0| \cos \chi)/c$, where v_0 is the unshifted frequency and χ is the angle between v₀ and k. If k is at an angle θ' with respect to E, the Doppler profile for fixed velocity photofragments at velocity v₀ has the functional form

$$I(\cos \chi) = (4\pi)^{-1} [1 + \beta P_2(\cos \theta') P_2(\cos \chi)].$$
(3)

Since $\cos \chi$ is proportional to the Doppler shift, Eq. (3) is the "normalized" Doppler line shape. In order to obtain an overall line shape for a velocity distribution, Eq. (3) is scaled by $|\mathbf{v}_0|$ and convoluted with the photofragment translational energy distribution P(E)dE. The usual approach is to assume that P(E) does not depend on χ . This calculated Doppler line shape can then be compared with the experimentally measured Doppler profile.

In Fig. 2 the measured Doppler profiles for the ${}^{1}P_{1}^{\circ} \leftarrow {}^{1}D_{2}$ and ${}^{3}D_{3}^{\circ} \leftarrow {}^{3}P_{2}$ lines are shown for the excimer polarizations parallel and perpendicular to the VUV axis. The measured laser line shape is also shown in Fig. 2. In order to fit a velocity distribution and value of β to the experimental data, we used the value of β as a variational parameter to minimize the chi-squared deviation for an assumed P(E), for each excimer polarization separately. If the β parameters for the two polarizations agreed within their standard deviations, the P(E) assumed was considered "acceptable." The reason for using the β parameter as a measure of the "goodness" of the fit to the data was twofold: convenience, as the P(E) does not necessarily have a convenient functional form, and also because the β parameter is strongly correlated with variations in P(E) for a given polarization. As a simple example, if the trial P(E) is weighted too strongly at large E_{trans} , and the true β parameter is greater than zero, the error in P(E) can be compensated by a smaller β for horizontally polarized light, as this will weight smaller values of $\cos \chi$ more, counteracting the shift of P(E) to larger E_{trans} . The same situation will result in a larger β param-



FIG. 2. Doppler profiles for $S({}^{1}D_{2})$ and $S({}^{3}P_{2})$ photoproducts. A typical laser line shape is shown in the first panel (dashed line), and the excimer laser polarization is with respect to the VUV probe laser axis. The asymmetry in the Doppler profile is caused by the asymmetric VUV probe line shape. Data points from several different experiments are given, and the calculated line shape is the solid line drawn through the points.

eter for a vertically polarized photolysis laser, as again smaller $\cos \chi$ values will be weighted more. This means that only a correctly balanced P(E) distribution will result in the same β parameter fitting both photolysis polarizations. Among the various acceptable velocity distributions for the $S(^{3}P)$ and $S(^{1}D)$ products, the two that gave the lowest chisquared were chosen, and these were used to calculate the fits to the data shown in Fig. 2.

The resultant translational energy distributions are shown in Fig. 3, where the range of acceptable distributions around the best fit are indicated by the shaded area. The β parameters fitted to the Doppler line shapes shown in Fig. 2 are $\beta = 0.85 \pm 0.15$ for the CS(${}^{1}\Sigma^{+}$) + S(${}^{3}P$) product channel and $\beta = 0.99 \pm 0.15$ for the CS(${}^{1}\Sigma^{+}$) + S(${}^{1}D$) product channel.

The observation of an anisotropy in the photofragment distribution, which was not observed in previous experiments,¹⁰ is due to the rotational cooling in the supersonic expansion. In order to estimate the temperature of the jet, expansions of CO/He and NO/He mixtures from the same



FIG. 3. Translational energy distributions for the singlet and triplet dissociation channels determined from the Doppler profiles in Fig. 2. Range of acceptable P(E) curves is indicated, along with a scale of CS(v) states corresponding to the amount of translational energy observed. The two distributions have been normalized to agree with the observed branching ratio.

source pressure were probed by LIF spectroscopy to determine the rotational temperatures. These temperatures were found to be around 20 K, and as both NO and CO have significantly larger rotational constants than CS_2 , one would expect the CS_2 rotational temperature to be no higher than that observed for CO or NO.

DISCUSSION

³P/¹D branching ratio

Our observed ratio $S(^{3}P)/$ branching of $S(^{1}D) = 2.8 \pm 0.25$ is in rough agreement with the results of state-sensitive S atom detection experiments in that the $S(^{3}P)$ is by far the major channel. The fact that the absolute value of the branching ratio is different is not surprising as all previous measurements relied on relaxation to provide a measure of the nascent relative ${}^{3}P/{}^{1}D$ population, while our measurement is a direct, collision-free determination whose main uncertainty is the relative line strengths for the transitions used to detect the $S(^{1}D)$ and $S(^{3}P_{2})$ products. The severe disagreement between our result and those of Yang et al.¹⁰ and McCrary et al.¹³ arise from the interpretation of the product time-of-flight data in these two previous studies. There is no distinction between reactions (1a) and (1b) in the product detection, so the interpretation of the time-offlight spectrum to obtain a ${}^{3}P/{}^{1}D$ branching requires a partitioning into two components corresponding to the two pathways. In both cases, the contribution of the triplet channel to the low energy part of the TOF spectrum has been underestimated, especially in the case of Yang et al., who assigned the entire low energy part of the spectrum (below 20 kcal/mol) to the singlet channel.

In a recent study, Kanamori and Hirota²⁶ used transient infrared absorption spectroscopy to detect the CS fragment from CS_2 photolysis, and concluded that the branching ratio between the singlet and triplet channels is "approximately one to one." The analysis of the transient absorption data is difficult, because the IR absorption measurements can only give population differences between adjacent vibrational levels, and so a detailed analysis of the Doppler line shapes was carried out in order to obtain information on the product energy distributions.

This procedure relied on the difference in Doppler shift between CS(v) and CS(v-1) products for both singlet and triplet channels, and was involved and quite uncertain for CS(v < 5) products. The difficulty arises since both singlet and triplet channels can produce these products and for the triplet channel products there is little difference between the Doppler profiles for CS(v) and CS(v-1). It appears that all CS products with less than 20 kcal/mol of internal energy were assigned to the singlet channel, while our results indicate that nearly half of these products correlate to the triplet channel.

In the experiments of Kanamori and Hirota the CS products suffered on the order of ten gas kinetic collisions during the observation time, thus reducing the certainty of any Doppler analysis. The 1:1 branching ratio quoted by Kanamori and Hirota can be viewed as a lower limit on the triplet product yield, and thus consistent with our measurements.

The only previous result which is in agreement with our branching ratio, that of Dornhöfer *et al.*,¹² is not derived from experimental data, but comes from their proposed resolution of the discrepancy between the branching ratios of Yang *et al.*¹⁰ and Addison *et al.*¹¹ While it is interesting to speculate on the role of secondary fragmentation of CS(v > 5) in previous photochemical studies, we feel that this is not the only cause for the large discrepancy between these two previous results.

The time-of-flight spectrum of Yang *et al.*¹⁰ is consistent with the energy distributions derived from our measurements, and does not appear to have been severely distorted by secondary photolysis of the CS. A correct partitioning of the TOF spectrum would have yielded a much higher branching into the triplet channel; this is the error in the analysis of Yang *et al.*¹⁰

Finally, we should stress that the major uncertainty in the current branching ratio is associated with the line strengths for the atomic S resonance lines. As mentioned in the last section, attempts to measure the relative line strengths have not provided more accurate values, but have indicated that the ${}^{1}P_{1} - {}^{1}D_{2}$ line strength may be too high. If this turns out to be the case, the triplet:singlet ratio will be reduced slightly, but preliminary results indicate that the ratio will not change dramatically from the current value of 2.8.

Energy release

Through Doppler spectroscopy on the $S(^{3}P)$ and $S(^{1}D)$ products, it is possible to unambiguously resolve the singlet and triplet channel energy release. It would appear from our results that a considerable fraction of the available energy, approximately 50%, is channeled into product vibration in both singlet and triplet channels, and that in both cases the product vibrational distribution is strongly inverted. These results are consistent with all previous work on CS₂, in which a large degree of vibrational excitation in the CS product has been found. In order to compare our results with those of others, where it has not been possible to separate the singlet and triplet channels, we added together the translational energy distribution given in Fig. 3, weighted by the ${}^{3}P/{}^{1}D = 2.8$ branching ratio. The resulting energy distribution is in reasonable agreement with that of Yang et al.¹⁰ and quite similar to that found by Ng and co-workers and Frey and co-workers in recent high resolution photofragment translational spectroscopy experiments.²⁷ In order to provide a comparison with laser-induced fluorescence results. our P(E)dE curves were divided according to vibrational state using the area of the P(E)dE curve between the energy limits corresponding to v and (v + 1). Although certainly not a definite measurement of the product vibrational distribution, this procedure should at least reflect the general features of the true product P(v) distribution. This division of the translational energy distribution is consistent with the results of Butler et al., 15 who found the CS photoproduct had on the order of 2 kcal/mol in rotational excitation. The P(v)distribution obtained from our data is shown in Fig. 4, along with those from previous LIF studies. Again, there is qualitative agreement between our results and previous work al-

CS VIBRATIONAL DISTRIBUTION



FIG. 4. Vibration distributions for the total CS product from both singlet and triplet channels. Present results, as described in the text, are plotted as squares. Previous results; circles, Ref. 13; triangles, Ref. 15; crosses, Ref. 10.

though our data would indicate relatively more product with v'' > 6 than previously seen.

A surprisal analysis of our P(v) distributions was performed, using the prior distribution given by Yang *et al.*¹⁰ For both channels, an essentially linear suprisal plot was obtained, in agreement with Yang *et al.*

As the excitation at 193 nm produces CS_2 in the ${}^{1}\Sigma_{u}^{+}({}^{1}B_2)$ state above the barrier to linearity,⁶ the photodissociation occurs from a quasilinear excited state. This results in a large degree of vibrational excitation in the CS, in contrast to the behavior that occurs in the photodissociation of OCS at 220 nm, where the excitation of a bent excited state results in a large amount of CO product rotation and little or no vibrational excitation.²⁸

Our results indicate that for both singlet and triplet pathways, the photofragmentation channels about 50% of the available energy into product vibration. For dissociation of linear ABC into A + BC products, the fraction of the available energy that will end up as vibration in the BC product is given by²⁹

$$\frac{E_{\rm vib}}{E_{\rm AVL}} = \frac{M_{\rm A}M_{\rm C}}{(M_{\rm A}+M_{\rm B})(M_{\rm B}+M_{\rm C})} \left| \int_0^\infty {\rm sech}^2(t)e^{i\lambda t} dt \right|^2,$$
(4)

where M_A , M_B , M_C are the masses of A, B, and C and $\lambda = 2\omega L/v_0$, where ω is the frequency of vibration for BC, $v_0 = [2 E_{AVL} (M_A + M_B)/M_A M_B]^{1/2}$ and L is the range parameter for the repulsion between A and B, which goes as $V(x) = V_0 e^{-x/L}$.

In the purely impulsive limit (i.e., as $L \rightarrow 0$), the integral goes to 1 and for CS₂ 53% of the available energy goes into vibration. As the repulsive potential is softened this fraction decreases. Thus, using an impulse model, one would conclude that the dissociation dynamics are the result of dissociation from a very repulsive surface in the collinear geometry. More sophisticated quantum mechanical models can also be used to calculate the energy release,³⁰ but these depend strongly on the choice of the repulsive potential.³¹ However, the repulsive potential is unknown in this case, and cannot be deduced from the spectrum, as the ${}^{1}\Sigma_{u}^{+}$ (${}^{1}B_{2}$) state of CS₂ is predissociating. It is known that the C–S bond length in the ${}^{1}\Sigma_{u}^{+}$ (${}^{1}B_{2}$) state, 1.66 Å, is significantly longer than in CS(${}^{1}\Sigma^{+}$), 1.54 Å.³² This also suggests that the product CS will be highly vibrationally excited^{30,33} using Franck– Condon arguments to estimate the product vibrational distribution.

It is interesting to note the similarity of the energy release in both triplet and singlet products. In both cases, the product vibration distributions are inverted, with about 50% of the available energy being channeled into vibrational excitation. The surprisal plots for both channels are linear, with similar slopes. These results imply that the dynamics of both channels are the same, involving a fairly repulsive energy release from a linear geometry.

Product recoil anisotropy

The Doppler profiles displayed in Fig. 2 show the anisotropy in the product recoil velocity angular distribution for both product channels. This anisotropy was not observed in the earlier molecular beam work of Yang *et al.*¹⁰ because they used an effusive, room temperature, beam of CS_2 while the present work was carried out in a supersonic beam.

The supersonic expansion relaxes the rotational distribution of the sample gas to a very low "temperature." The classical rotational period is given by $\tau_{\rm rot} = (I/2kT)^{1/2}$, where I is the moment of inertia and T is the rotational temperature. The room temperature rotation time for the ${}^{1}\Sigma_{\mu}^{+}$ (${}^{1}B_{2}$) state of CS₂ is 0.6 ps, and since Yang *et al.* did not observe any anisotropy in the angular distribution of photoproducts they concluded that the ${}^{1}\Sigma_{\mu}^{+}({}^{1}B_{2})$ state lifetime was 1 ps. In our experiments, the CS₂ rotational temperature is about 20 K, and thus the rotation time in our case is 2.3 ps, or about a factor of 4 longer than at room temperature. At this lower temperature, the estimated 1 ps dissociation lifetime is less than the rotational period, resulting in the observed product angular anisotropy. From our observed β parameters, an estimate can be made of the dissociation lifetime for excited CS₂, using the theory of Yang and Bersohn.34

For dissociation of linear molecules, the β parameter is given by³⁴

$$\beta = \frac{1}{2} P_2[\mu(0)] P_2[\mathbf{D}(0)] \left(1 + 3\gamma \, e^{\gamma} \int_{\infty}^{\gamma} \frac{e^{-v}}{v} dv\right), (5)$$

where $\gamma = I/(8kT\tau^2)$ with τ being the dissociation lifetime. For dissociation of the ${}^{1}\Sigma_{u}^{+}({}^{1}B_{2})$ state of CS₂, $P_{2}[\mu(0)] = 1$ and $P_{2}[(\mathbf{D}(0)] = 1$. Using Eq. (5), with T = 20 K, a β parameter of 0.9 corresponds to a ${}^{1}\Sigma_{u}^{+}({}^{1}B_{2})$ lifetime of about 2 ps. This "lifetime" is only an estimate, as the Boltzmann averaging used to obtain Eq. (5) will not be completely accurate for the rotational distribution in the supersonic beam, which is non-Boltzmann.

The large amount of bending excitation in the CS₂ will also have a small effect on β , as bending vibrations reduce β

from the limit of 2 for parallel transitions.³⁵ As the dissociating CS₂ is in a quasilinear excited state, the treatment of Morse and Freed for linear molecules³⁵ can be used. Their treatment accounts for the displacement of the equilibrium principal axis of inertia (which is viewed as the transition dipole axis) and the recoil vector that is induced by bending vibrations. While this effect is very pronounced in molecules such as HCN, where the departing H atom undergoes large amplitude motion in the bending vibration, the mass combination in CS₂ minimizes this effect. Using the theory of Morse and Freed, we calculate that 13 quanta in the 426 cm^{-1} bending vibration in the excited state CS₂ will have less than a 1% effect on B. Even if one considers the extreme case of a distribution of CS2 geometries with bond angles between 180° and 150° with the transition dipole fixed along the unbroken CS bond, the resulting β is reduced by only 10%.

The estimated dissociation lifetime is consistent with previous estimates for the lifetime of the excited state CS₂ prepared by 193 nm pumping. The linewidth for the vibrational bands in the 193 nm range observed in the absorption spectrum of jet cooled CS₂⁶ was less than 20 cm⁻¹, including the instrumental linewidth, and any residual inhomogeneous broadening. This implies a lower limit of 0.3 ps for the excited state lifetime, and probably a significantly longer lifetime than 0.3 ps. Fluorescence yield measurements also indicate a lifetime on the order of 1 ps for the ${}^{1}\Sigma_{u}^{+}({}^{1}B_{2})$ state when 200 nm excitation is used⁵ and Yang *et al.* claim the isotropic product recoil observed for 300 K CS₂ indicates a dissociation lifetime longer than the 0.6 ps rotational period.

Our ability to measure the β parameter, which provides more definitive data on the dissociation lifetime of CS_2 shows the advantage of using supersonically cooled samples in photofragment spectroscopy.

Nonadiabatic dynamics

The final question that needs to be addressed is the reason for the dominance of the "spin-forbidden" triplet channel in the 193 nm photodissociation of CS_2 . Although the spectroscopy of the ${}^{1}\Sigma_{u}^{+}({}^{1}B_2)$ state is not fully understood, the large oscillator strength for the transition would indicate that the state excited at 193 nm is essentially a pure singlet state, coupled fairly strongly with a dissociating state which leads to CS + S products. The observation of triplet products indicates that there must be a spin-orbit coupling with a dissociating states were strongly coupled, one might expect a statistical ${}^{3}P/{}^{1}D$ branching ratio of 16.4.³⁶

The existence of this spin-orbit coupling can be seen in the absorption spectrum of CS₂, where absorption bands due to transitions to excited triplet states are observed. Of particular interest here is a fairly strong absorption at 182 nm, which has been assigned by Greening and King³⁷ as being due to a ${}^{3}\Sigma_{u}^{-}$ excited state. This state correlates with the CS(${}^{1}\Sigma^{+}$) + S(${}^{3}P$) products, so it may be involved in the photodissociation process, though not through direct excitation.

The strong coupling between the ${}^{3}\Sigma_{u}^{-}$ and ${}^{1}\Sigma_{u}^{+}$ states is shown by the strength of the triplet-singlet transition at 182 nm which is allowed as a result of "intensity borrowing" from the nearby fully allowed ${}^{1}\Sigma_{u}^{+} - {}^{1}\Sigma_{g}^{+}$ transition.³⁷ This means that the excited state of CS₂ pumped at 193 nm has some triplet state character, and is coupled to a dissociating triplet state.

This coupling to the triplet state is not restricted to the CS_2 molecule, but will continue as the CS and S products separate. Two alternate pictures can then be used to explain the high yield of triplet product. The first is that the triplet character of the initially pumped excited state, combined with the density of states weighting in favor of triplet products, is responsible for the preponderance of the triplet channel. The second possible view is that coupling in the exit channel is more important, and nonadiabatic interactions as the photofragments separate lead to the product branching.

In a naive one-dimensional picture based on this second model, one can imagine a curve crossing occurring between the initial CS_2 singlet and triplet potentials, leading to a pair of adiabatic potentials, with the lowest energy one resulting in $CS + S({}^{3}P)$ products. In this picture, the triplet product is then the result of the adiabatic dissociation, and becomes the major product. In three dimensions, the interaction between surfaces is much more complicated than a simple avoided crossing,³⁸ but the same idea still applies, with the lower energy surface leading to triplet products.

In any case, the lifetime of the excited state CS_2 and the product energy distribution are determined very early in the dissociation, and are the same for both triplet and singlet channels, while the singlet:triplet branching ratio is determined by spin-orbit coupling between dissociating singlet and triplet surfaces.

CONCLUSIONS

The purpose of the experiments outlined in this paper was to study the dynamics of the 193 nm photolysis of CS_2 under collision-free conditions. In these experiments, the S atom product was detected by laser-induced fluorescence, with the S(³P) products being detected separately from the S(¹D) ones. This direct product detection provided a resolution of the controversy over the singlet-triplet branching ratio, which was found to be S(³P)/S(¹D) = 2.8 ± 0.3.

By analyzing the Doppler profile of the S product LIF lines, the detailed photofragmentation dynamics of the singlet and triplet channels could be studied independently. This analysis showed that for both singlet and triplet channels, 50% of the available energy was channeled into internal excitation of the CS product, with the CS being formed in a strongly inverted vibrational distribution.

In contrast with previous photofragment spectroscopy experiments, an anisotropy was observed in the product angular distribution and it was the same in both singlet and triplet channels. The reason for the observation of anisotropy in this work was the use of a supersonic CS_2 beam, which cooled the CS_2 rotation. The anisotropy observed is consistent with a predissociating excited state with a 2 ps lifetime.

The picture of the dynamics that emerges is one in which the initially pumped quasilinear excited state predissociates, channeling the available energy into product vibration through a very repulsive energy release in a collinear geometry. Spin-orbit coupling between two adiabatic surfaces, one correlated with singlet products, and the other with triplet products, results in the observed dominance of the triplet product channel.

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