



Product energy disposal in the nonadiabatic reaction S(1 D)+CS2 \rightarrow S2 (X 3Σ- g)+CS (X 1Σ+)

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Product energy disposal in the nonadiabatic reaction $S(^{1}D)+CS_{2} \rightarrow S_{2} (X^{3}\Sigma_{\alpha}^{-})+CS (X^{1}\Sigma^{+})$

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The product energy disposal in the reaction $S(^{1}D) + CS_{2} \rightarrow S_{2} + CS$ is measured via laserinduced fluorescence. Molecular sulphur is produced exclusively in its electronic ground state $({}^{3}\Sigma_{c}^{-})$ with up to 3 quanta of vibrational excitation and rotational excitation that roughly approximates a 1000 K Boltzmann distribution. The CS produced from the reaction is formed predominantly in its vibrationless state. The total internal energy content of the product molecular sulphur is only about 12% of the total available energy of the reaction; the CS fragment also has minimal internal energy, implying that most of the reaction energy resides in product translation. These results are different from those observed in the isovalent S + OCSreaction and suggest that a different detailed mechanism is operative.

INTRODUCTION

Recently, observation of we reported the S₂ ($X^{3}\Sigma_{g}^{-}; v \leq 2$) from 308 nm irradiation of low pressures of CS_2 .^{1(a)} We concluded that the S_2 is formed in a chemical reaction between CS2 molecules and "hot" S atoms generated via two-photon absorption in CS2. However, the 154 nm photodissociation of CS₂ gives rise to an unknown distribution of S-atom electronic states. Therefore, we report here a study of the dynamics of the reaction under conditions in which the initial electronic and translational energy distributions of the sulphur atom are well characterized, using 193 nm photodissociation of CS_2 as the S-atom source.² Additionally by performing the experiment in a large excess of buffer gas to translationally "cool" the atoms, the dynamics of electronically excited S-atom reactions may be differentiated from those involving translational energy.

Though the reactions of excited sulfur atoms have been documented for some time,³ there are almost no reports of the dynamics, and specifically the product state distributions, of these reactions. By analogy to the reactions of electronically excited oxygen atoms, $O(^{1}D)$, one expects that the reactions of $S(^{1}D)$ might involve the formation of a longlived intermediate complex. Indeed, this is implied by the products of its reactions,³ the large quenching cross section^{4,5} and what is known about its product energy disposal.^{6,7} Two studies which have reported product internal state distributions involve the $S(^{1}D) + OCS$ reaction system, which produces diatomic sulphur in both the ground $(X^{3}\Sigma_{g}^{-})$ and excited $(a^{1}\Delta_{g})$ states.^{6,7} Since the CS₂ and OCS molecules are isovalent, one would guess that very similar dynamics would govern their reactions with $S(^{1}D)$. However, we find that there are significant differences in the dynamics of these two systems. The dynamics of the title reaction may be more closely related to those of the $O(^{1}D) + CO_{2}$ reaction.

Three sets of experiments are performed to elucidate the complete energy disposal in the title reaction. The major portion of this work interrogates the vibrational and rotational state distributions of ground state molecular sulphur, S₂ ($X^{3}\Sigma_{g}^{-}$), through LIF on the ($B^{3}\Sigma_{u}^{-} \leftarrow X^{3}\Sigma_{g}^{-}$) transition. The second study attempts to observe electronically excited molecular sulphur, $S_2(a^{1}\Delta_g)$ through the $(f^{1}\Delta_{\mu} \leftarrow a^{1}\Delta_{\alpha})$ transition. The final study obtains LIF spectra (through the CS $A^{\dagger}\Pi \leftarrow X^{\dagger}\Sigma_{g}$ transition) of the CS $(X^{T}\Pi)$, also produced in the reaction of $S(^{T}D) + CS_{2}$.

EXPERIMENT

The experimental apparatus is depicted in Fig. 1. The photoinduced reactions are carried out in a 1 in. diam cylindrical pyrex flow cell equipped with suprasil windows and evacuated through a 77 K trap by a 5 CFM mechanical pump. Typically, the cell is filled with He buffer gas at a pressure of 2-10 Torr. Under these conditions, the cell evacuation time is about 5 ms, ensuring that all chemical products are removed between the 10-20 Hz laser shots. A small pressure $(1-50 \times 10^{-3} \text{ Torr})$ of degassed reagent grade CS₂ is introduced separately into the cell through a needle valve. The He buffer gas is not used in experiments which probe the product rotational quantum states. The pressures are measured using a capacitance manometer and the He buffer flow is regulated using a mass flowmeter.

The $S(^{1}D)$ reagent is produced by the photodissociation of CS_2 using the unfocussed and strongly attenuated beam of an ArF (193 nm) excimer laser. Excimer laser pulse energies range from 100 to 500 μ J/pulse in a 1 mm diam beam (1.25 MW/cm²). The CS products from the initial photodissociation and CS and S₂ products of the subsequent chemical reaction are detected via laser-induced fluorescence (LIF) excited by the unfocussed, frequency doubled output

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FIG. 1. Schematic of experimental setup. Key: A =attenuator; BC =boxcar integrator; COMP = computer; DG = digital delay generator; DU = autotracking frequency doubler and harmonic separator unit; EM = laser energy meter; F = 193 nm blocking filter; G = reagent and buffer gas inlets; L = collecting lens; P = pumpout port; PD = photodiode trigger; PMT = photomultiplier tube.

of a counterpropagating Nd:YAG-pumped tunable dye laser. The 0.1 cm⁻¹ resolution dye laser is operated in the wavelength range 570-625 nm for ground state S₂ detection. A second dye laser, with 0.5 cm^{-1} resolution, is used in the wavelength range 500-530 nm to detect electronically excited S_2 and ground state CS. The pulse energy of the doubled dye laser in each wavelength region is $\sim 100 \,\mu\text{J/pulse}$ in a spot size of 0.02 cm². A digital pulse generator is used to control the delay between the photolysis (pump) and probe lasers. During the experiment, pump-probe delays range from 1–1000 μ s. The optimal delay time is determined by locating a bandhead of v = 1 at a long delay time, then decreasing the delay between lasers to shorter times until the threshold for detectable signal is reached. At delay times that correspond to significantly less than one gas kinetic collision (~ 0.1) only very weak S₂ signal is observed. At zero and negative delay times (probe before pump) no S_2 signal is observed. These results show that the cell is free of products from previous laser shots. Laser pulse energies are measured continuously during each run by commercial laser power meters. All spectra are taken in the limit where the LIF signal behaves linearly with the probe laser energy, since it is possible to achieve saturation at energies as low as 500 μ J/pulse. The LIF from the reaction products is imaged with a 7 cm focal length, f/3 Suprasil lens through a 193 nm blocking filter onto a photomultiplier tube (PMT). The unamplified PMT signal and the simultaneously measured probe laser intensity are sent to a boxcar averager, processed and directed to a laboratory computer for storage and further analysis. Typically the signals from 10-30 laser shots are averaged together to improve the signal-to-noise ratio; this results in an effective resolution of 1 cm^{-1} . The spectra used in extracting relative populations are all normalized for the probe laser energy. Since the pump laser energy varies less than 10% over the course of a measurement, it is treated as a constant.

DATA ANALYSIS

Due to the complexity of the S_2 $(B^{3}\Sigma_{u}^{-} \leftarrow X^{3}\Sigma_{g}^{-})$ transition, an exact fit to the measured spectrum is not possible. Therefore, to analyze the product state distributions of S_2 $(X^{3}\Sigma_{g}^{-})$, we generate a series of simulations of the experimentally obtained spectra. These simulations assume a Boltzmann distribution in rotation and have the rotational temperature and the relative populations of the vibrational levels as parameters. By using large pressures of He in addition to the CS_2 , the rotational distribution of the S_2 $(X^{3}\Sigma_{g}^{-})$ product is forced into a Boltzmann distribution at a temperature of 300 K, reducing the parameters to just the relative populations of vibrational states. Simulated spectra are visually compared with the experimental data to obtain a semiquantitative value for the initial relative vibrational populations.

The vibrational structure of the S₂ $(B^{3}\Sigma_{u}^{-} \leftarrow X^{3}\Sigma_{g}^{-})$ transition is calculated using the standard formulae for vibronic structure found in Herzberg,⁸ using ground and excited state constants ω_{e} and $\omega_{e}x_{e}$ given in Huber and Herzberg.⁹ The Franck–Condon factors for the *B*–*X* transition are taken from Anderson *et al.*¹⁰ The rotational structure is calculated using the energy level formulas for a ${}^{3}\Sigma$ state in Hund's case (b) given by Hougen.¹¹ The energy levels are

$$F_{1}(K) = BK(K+1) + (2K+3)B - \lambda$$

- $[\lambda^{2} - 2B\lambda + B^{2}(2K+3)^{2}]^{1/2}$
+ $\gamma(K+1) + \gamma/2$,
$$F_{2}(K) = BK(K+1),$$

$$F_{3}(K) = BK(K+1) - (2K-1)B - \lambda$$

+ $[\lambda^{2} - 2B\lambda + B^{2}(2K-1)^{2}]^{1/2} - \gamma K + \gamma/2$.

The terms correspond to the three J components: J = K + 1, J = K, and J = K - 1, respectively. γ is the spin-rotation coupling constant and λ is the spin-spin interaction constant. Since both the ground and excited states have ${}^{3}\Sigma_{g}^{-}$ symmetry, there are six main branches $(P_{1}, P_{2}, P_{3}, R_{1}, R_{2}, R_{3})$ and six satellite branches $({}^{P}Q_{23}, {}^{P}Q_{12}, {}^{P}R_{13}, {}^{R}Q_{21}, {}^{R}Q_{32}, {}^{R}P_{31})$ allowed. Two forbidden branches, ${}^{N}P_{13}$ and ${}^{T}R_{31}$, may also be present. Figure 2 displays a room temperature spectrum of S₂ with all the branch assignments identified.

The ground and excited state values for the constants B, γ and λ are given in Huber and Herzberg.⁹ All these constants show a vibrational state dependence and are expressed as a series expansion in the vibrational quantum number. The excited state λ values are not as well known as those of the ground state because there is a perurbation in the excited state caused by a near-lying ${}^{3}\Pi_{u}$ state.¹² This perturbation results in the appearance of additional lines (up to 20) in the spectrum and a modification of the spectral intensities. The λ values are + 9.5 for odd v levels (v = 1,3,5) and -4.7 for the even levels (v = 0,2,4), with λ for v = 6 and v = 7 also believed to be negative.^{9,11,13} Strictly speaking, the magnitude of λ places the description of this transition in the intermediate regime between Hund's case (a) and case (b). Therefore, we use rotational line strengths (Hönl-London

Relative Intensity



FIG. 2. Excitation spectrum of the (5–0) band (e.g., from v = 0 in the ground state to v = 5 in the excited state) of the S_2 $(B^3 \Sigma_u^- + X^3 \Sigma_g^-)$ transition measured under conditions such that the rotations are relaxed to a 300 K thermal distribution. The 14 branches as calculated are indicated above the spectrum. Both main branch and satellite branch transitions are shown. The labels designate ${}^{(\Delta K)}\Delta J_{F'(F'')}$, where the bracketed terms are not given for the main branch transitions. For example, ${}^{R}Q_{32}$ designates a transition with $\Delta K = +1$, $\Delta J = 0$, $F' = F_3$, and $F'' = F_2$. P₁ designates a transition with $\Delta K = \Delta J = -1$; $F' = F'' = F_2$. See Refs. 8 and 14 for details.

factors) obtained from the work of Tatum and Watson¹⁴ for the intermediate case (a)-case (b) coupling.

Because of the perturbation the S₂ B state, we (and the authors of Ref. 6) do not obtain a quantitative match between the experimentally obtained spectra and the simulations. To check our calculation, we fit the energetically next higher S₂ transition, $C^{3}\Sigma_{u}^{-} \leftarrow X^{3}\Sigma_{g}^{-}$, using as experimental

data the plate spectra of Barrow *et al.*¹⁵ The C state is not known to be perturbed; the energy level match between the measured spectrum and our fit (using constants from Ref. 9) is accurate to within ~1 cm⁻¹. In spite of not having exact formulations for the intensities, Fig. 2 demonstrates that we can semiquantitatively assign the rotational structure of the S₂ $(B^{3}\Sigma_{u}^{-} \leftarrow X^{3}\Sigma_{g}^{-})$ transition at room temperature.

RESULTS

The photolysis of CS_2 at 193 nm results in the production of CS and atomic sulphur in both the ground $({}^{3}P)$ state and the excited $({}^{1}D)$ state, with a branching ratio of $\sim 3:1$ in favor of the triplet.² The photolysis deposits about half of the available energy, \sim 45 and 19 kcal mol⁻¹, respectively, into translation in each channel. The channel which is the main contributor to the production of $S_2(X^3\Sigma_{e}^{-})$ is determined by using large pressures of He (or Ar, or N_2) as a buffer gas in order to collisionally relax the initial translational energy to 300 K. At 300 K the reaction of $S({}^{3}P)$ is slow¹⁶ and slightly endoergic;¹⁷ no vibrationally excited S_2 will be formed. However, we observe vibrationally excited product, indicating that the reaction involves electronically excited S atoms. Furthermore, the measured appearance rates of S_2 in v = 0, 1, and 2 are identical, and correspond to a near gas-kinetic reaction rate with CS₂ ($k \simeq 10^{-10}$ cm³ molecule⁻¹ s⁻¹). The rate constant for reaction of $S(^{1}D)$ with CS₂ has been reported to be near gas kinetic,⁴ in agreement with our results.

Figure 3 shows a spectrum of ground state S_2 obtained with 0.045 Torr of CS_2 in a bath of 5 Torr He at a delay time of 1.5 μ s between the pump and probe lasers. Transitions originating from v levels 0, 1, and 2 are clearly observed in this wavelength region. At different wavelengths, traces of signal due to population in v = 3 are also seen. Higher-lying



FIG. 3. Part of the S₂ $(B^{3}\Sigma_{u}^{-} \leftarrow X^{3}\Sigma_{s}^{-})$ excitation spectrum measured via LIF. For this trace, 45 mTorr of CS₂ and 5 Torr of He buffer are used; the delay time between the lasers is 1.5 μ s. These conditions ensure that rotational relaxation is complete, but that the vibrational distribution remains the initial one. The vibronic bands are labelled (v', v'')above their respective bandheads. A transition from vibrationally excited CS product of the CS₂ photolysis is also seen in this wavelength region.

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vibrational levels have poorer Franck–Condon overlaps and are not detected. The presence of buffer gas ensures that rotational relaxation (as well as translational slowdown) is complete on the timescale of the measurement. Therefore, all spectra taken under these conditions display a Boltzmann rotational distribution corresponding to 300 K (see Fig. 2). However, since He is very inefficient at relaxing S₂ vibrations,^{1(b)} the spectrum in Fig. 3 (and other similar spectra) represents the initial vibrational distribution of the product. The relative populations of the S₂ vibrational levels are obtained by creating simulated spectra, using a 300 K rotational distribution and the relative populations as a variable. By performing many such simulations, to match a variety of different experimental conditions, we are able to construct the following initial vibrational distribution:

 $v = 0/1/2/3::1.0/0.25 \pm 0.05/0.1 \pm 0.05/(\text{trace}).$

A spectral simulation with this vibrational distribution is depicted in Fig. 4, as well as a spectrum measured under conditions identical to those of Fig. 3. This distribution approximates a Boltzmann distribution with a "vibrational temperature" of 900 K; the average energy in S_2 vibration is



FIG. 4. (a) An experimentally measured S₂ ($B^{3}\Sigma_{\mu} \leftarrow X^{3}\Sigma_{\mu}^{-}$) LIF spectrum measured under the same conditions as that shown in Fig. 3. (b) A simulation of the spectrum, using $T_{rot} = 300$ K and a vibrational distribution v = 0/1/2 = 1.0/0.25/0.10. See the text for details.

thus about 1 kcal mol⁻¹. The present result is quite similar to that reported in Ref. 1, for reaction of S atoms produced via 154 nm photolysis of CS_2 . Thus it appears that $S(^1D)$ is a significant product of that dissociation as well.

Figures 5(a)-5(d) show a comparison between an unrelaxed spectrum (a), obtained at the shortest delay times and with no buffer gas present, and simulations using the vibrational distribution given above and rotational temperatures of (b) 500 K, (c) 1000 K, (d) 2000 K. Although none of the simulated spectra are identical to the experimental one, the simulation at 1000 K reproduces the gross features

quite well. Thus, within the limitations of our analysis, the rotational distribution is non-Boltzmann, but appears similar to a Boltzmann distribution at 1000 K. This temperature corresponds to an average rotational energy of 2 kcal mol⁻¹.

It is of some interest to explore the effect which translational energy in the S atom might have on the energy disposal. This information is contained in the comparison between the vibrational distributions observed in the presence and absence of buffer gas. The result of the experiment in the absence of buffer is shown in Fig. 5(a). The relative intensities of the vibronic features are the same as shown in Figs. 3



FIG. 5. (a) Experimental spectrum of S_2 $(B^3\Sigma_u^- \leftarrow X^3\Sigma_s^-)$ measured in the absence of He buffer gas. (b) A simulation using the vibrational distribution of the previous figure and $T_{rot} = 500$ K. (c) as (b), but $T_{rot} = 1000$ K. (d) $T_{rot} = 2000$ K.



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and 4. A complication to this approach is the fact that under these conditions, it is energetically possible for ground state S atoms to react; this reaction could also produce S_2 ($X^{3}\Sigma_{g}^{-}$) in many vibrational levels. However, our results show that the vibrational distribution does not change significantly whether photolysis is carried out under neat or He buffer gas conditions, although the relaxation of the rotational distribution to a room temperature distribution is obvious.

The work of van Veen *et al.*⁶ demonstrated that in addition to S₂ $(X^{3}\Sigma_{g}^{-})$, S₂ $(a^{1}\Delta_{g})$ is produced from the reaction S(¹D) + OCS. Since OCS is isovalent with CS₂, it is reasonable to expect that the spin-allowed product, S₂ $(a^{1}\Delta_{g})$, is also produced from S(¹D) + CS₂. S₂ $(a^{1}\Delta_{g})$ can be observed by exciting the S₂ $(f^{1}\Delta_{u} - a^{1}\Delta_{g})$ transition, which in part occurs over the range 250-285 nm. Due to poor Franck-Condon factors, many of the bands appear only weakly, the most intense belonging to the v > 0 transitions. van Veen *et al.*⁶ report a strong transition occurring at approximately 264 nm, corresponding to the S₂ $(f^{1}\Delta_{u}v = 5 - a^{1}\Delta_{g}v = 1)$ absorption.

In our experiments on $S + CS_2$ no signal attributable to S_2 $(a^{1}\Delta_g)$ is observed in this wavelength region, though this product is readily seen when we dissociate OCS at 248 nm, as in Ref. 6. An absolute determination of the yield of elecronically excited S_2 is very difficult because CS_2 photodissociation results in the formation of vibrationally excited CS, whose (A-X) transitions occur in the same spectral region as the S_2 $(f^{1}\Delta_{\mu} \leftarrow a^{1}\Delta_{g})$ transition. However, based on our measured LIF intensities and the reported absorption cross sections¹⁸ for CS_2 at 193 nm and OCS at 248 nm, we estimate an upper limit to the S_2 $(a^{1}\Delta_{g})$ production of roughly 50–100 times less than that of S_2 $(X^{3}\Sigma_{g}^{-})$.

The second product from the title reaction is CS. Obtaining information about this product is complicated by the fact that CS is also a product of the initial photodissociation of CS₂ by the 193 nm light. We are able to make a qualitative estimate of the vibrational energy content of CS ($X^{1}\Sigma^{+}$) by observing the difference in the vibrational distributions of CS $(X'\Sigma^+)$ measured at times before reaction can occur, and that which is obtained at later times, following the reaction of $S + CS_2$. The measurement depends on the result^{1(a),1(b)} that CS (v > 0) relaxes fairly slowly (≥ 100 collisions) in the presence of CS_2 . This means that changes to the initial vibrational distribution of CS on the timescale of the chemical reaction can be attributed almost exclusively to reaction, rather than vibrational relaxation. The only significant increase (to within about a 10% error estimate) in CS population with time which we measure using either 193 or 308 nm 2-photon excitation of CS₂ occurs in v = 0. Therefore we conclude that any population in higher v levels amounts to less than 10% of that in v = 0.

DISCUSSION

The results may be summarized as follows: the reaction between $S(^1D)$ and CS_2 produces exclusively S_2 $(X \, {}^3\Sigma_g^-) + CS$ product; no $S_2 \, (a \, {}^1\Delta_g)$ is observed. The S_2 is born in v levels 0–3 with a distribution approximately Boltzmann at 900 K; the CS appears in v = 0 only. The rotational distribution in the S₂ product is non-Boltzmann, but approximates a "temperature" of 1000 K. Thus very little of the reaction exoergicity ends up in the internal degrees of freedom of the products. The total fraction of energy which appears in product vibration, rotation and electronic excitation is < 0.2. Therefore, more than 80% of the reaction energy is released as relative translation in the products.

The very large rate constant reported for the total loss rate of $S({}^{1}D)$ by Addison *et al.*⁴ is suggestive of "entrance channel control" in the deactivation.⁵ This mechanism requires a long-lived, bound reaction intermediate CS₃ in which trajectories become trapped. The trapping of trajectories allows them to sample any accessible surface crossings many times, increasing the probability of a nonadiabatic transition.¹⁹ Such a bound species is known for CO₃,²⁰ and is believed to be responsible for the rapid deactivation rate of $O({}^{1}D)$ by CO₂.²¹ A bound intermediate has been postulated to exist in OCS₂ as well.⁶ Recent *ab initio* results^{22,23} also predict a bound singlet CS₃ species, consistent with a recent experimental report.²²

A common outcome of reactions which proceed through long-lived complexes is a product vibrational distribution which, like that reported above, exhibits a strong monotonic decrease in population with v level. Even when a reaction is very exoergic, as is the case in many atom/radical reactions, little of the available energy may be channelled into vibration in the products.^{24,25} The reason for this is that in the breakup of a long-lived intermediate complex the available energy is often partitioned statistically among all of the accessible degrees of freedom. Since vibrations typically occupy only a small volume of phase space in these systems the fraction of total energy ending up as product vibration is generally small.

Since the vibrational distribution in the S₂ $(X^{3}\Sigma_{g}^{-})$ does display a monotonic decrease with v level, it might indicate a statistical breakup of the CS₃ complex. To explore this possibility we carry out a surprisal analysis, using a prior distribution for the S₂ given by²⁶ $P^{0}(f_{v}) = 2/9(1 - f_{v})^{7/2}$. The surprisal plot $(-\ln [P_v/P^o] vs f_v)$ is linear, with slope $\lambda_n = +13$. In the RRHO approximation used in this calculation, a "true" statistical distribution would yield a value of zero for λ_{v} . A large, positive value such as + 13 for the vibrational surprisal is usually associated with a considerably less-than-statistical disposal of available energy into vibration.²⁷ This is often the case in the CD product, with the "old" bond, in $A + BCD \rightarrow AB + CD$ type reactions. However, in the present instance, the S₂ bond is being formed in the reaction; one expects some preferential partitioning of energy into it. The surprisal result suggests that there are dynamical constraints operative, even though the reaction probably involves a long-lived CS₃ intermediate.

In this respect, the present results are reminiscent of those reported for the isovalent $S(^1D) + OCS$ reaction.^{6,7} In that case too, the reaction partitions a smaller amount of energy into the $S_2(X^3\Sigma_g^-)$ vibration than would be predicted by a statistical model. Bersohn and co-workers⁶ postulated that this was a dynamical consequence of the location of the singlet-triplet surface crossing region of the long-lived

 OCS_2 complex. In their model, this region has C_{2v} geometry with an S₂ bondlength almost identical to that in the free molecule. Switching from the attractive singlet surface to a repulsive triplet surface then gives rise to a repulsive force between the centers of mass of the nascent products, with no resulting vibration in the S₂. The model further predicts very little rotational excitation in the S₂, a feature which also is observed experimentally.

However, there are large and qualitative differences between our results and those of van Veen *et al.*,⁶ which mitigate against using the same model here. In the present case there is substantially more energy deposited into S_2 $(X^{3}\Sigma_{g}^{-})$ vibration and rotation than in the OCS reaction; also there is no S_2 $(a^{1}\Delta_g)$ formed in the CS₂ reaction, again in contrast to OCS. Since the S_2 $(a^{1}\Delta_g)$ product is both spin and energetically allowed in $S(^{1}D) + CS_2$, there must also be a more efficient nonadiabatic mechanism operative in the CS₂ reaction than in OCS.

The high cross sections for atomic quenching and for reaction imply that a long-lived CS₃ intermediate plays a role in both processes. The dynamics of S₂ formation will thus be governed by the unimolecular decomposition of this species. Since the available energy is not partitioned statistically among all the available states there must be dynamical "bottlenecks" which control the product energy disposal. Both the singlet-triplet surface crossing region and the transition state(s) (TS) for the formation of S₂ ($X^{3}\Sigma_{g}^{-}$) + CS are of particular importance as possible bottlenecks. We may use the observed energy disposal to describe these features on model singlet and triplet potential energy surfaces.

By analogy to the $O({}^{1}D, {}^{3}P) + CO_{2}$ system,²¹ there is probably a high barrier to the decomposition of CS₃ on the singlet potential energy surface (PES), yielding S₂ $(a {}^{1}\Delta_{g}) + CS(X {}^{1}\Sigma^{+})$, whose height might approach the reagent energy. We postulate that this transition state is bent, and occurs "late" along the reaction coordinate, with C-S and S-S bond lengths close to those of the free products. Furthermore, we suggest that a singlet-triplet surface crossing occurs at or near the crest of this barrier and that the triplet surface is uniformly repulsive after this TS. On this surface the energy released as the products separate will thus be predominantly into relative translation. A sketch of these model surfaces is shown in Fig. 6.

These features on the potential energy surfaces can ex-



plain all the observed results. The total $S(^{1}D)$ loss rate is controlled by the highly attractive nature of the singlet surface; almost every trajectory finds itself in the CS₃ well. Some of these trajectories encounter a crossing seam which gives rise to $S(^{3}P) + CS_{2}$ product, which we do not measure. Others continue on the singlet surface and find the TS described above, which correlates with S₂ $(a^{1}\Delta_{g}) + CS$ products. However, there is a nonadiabatic surface crossing at or near this TS, onto a triplet PES which correlates with S₂ $(X^{3}\Sigma_{e}^{-})$ + CS products. The efficiency of surface hopping for trajectories which access the TS must be unity; we observe that no singlet products are formed. This high probability arises because of the position of the crossing: at the barrier crest, the system has little translational energy; this can lead to high efficiencies in nonadiabatic transitions.²⁸ The system thus finds itself on the triplet PES with nearequilibrium bond distances in the S_2 and CS moeities; the energy release is then mostly into relative translation of the two fragments. Since the TS is bent, there is some torque generated in the nascent CS and S2 molecules; this evolves into product rotation.

These inferences are substantiated by recent preliminary *ab initio* results on the $S({}^{3}P, {}^{1}D) + CS_{2}$ system.²³ In these calculations, which include electron correlation effects at the MP2 level, there is a global minimum on the singlet surface, but only very shallow wells on the triplet. A planar, bent SCSS transition state for decomposition into CS and S_{2} products exists on both surfaces, with CS and S_{2} bondlengths very close to the free molecule values. The transition state energies on the triplet and singlet surfaces lie very close to one another; to within the error of the calculation they are essentially at the same energy. This energy lies just slightly below the reagent energy on the singlet surface. These results strongly support the dynamical model presented above, which is based purely on the empirical results.

CONCLUSIONS

We have measured the product energy partitioning in the reaction $S({}^{1}D) + CS_{2} \rightarrow S_{2} + CS$. The sulfur product is born exclusively in its ground electronic state $({}^{3}\Sigma_{g}^{-})$ with ~1 kcal mol⁻¹ in vibration and 2 kcal mol⁻¹ in rotation. The CS product is formed vibrationally unexcited. These results suggest that the dynamics are controlled by an efficient singlet-triplet surface crossing, lying near the transition state for product formation. This transition state probably occurs "late" along the reaction path, when the nascent products have assumed geometries close to those of separated products. These suggestions are supported by *ab initio* calculations of the relevant potential energy surfaces.

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Sapers, Andraos, and Donaldson: $S(^{1}D) + CS_{2} \rightarrow S_{2}(X^{3}\Sigma_{a}^{-}) + CS(X^{1}\Sigma^{+})$

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