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Laser fluorescence study of the $S(^{1}D) + CD_{4}$ reaction: determination of the SD product internal state distribution

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Abstract

The dynamics of the $S(^{1}D) + CD_{4} \rightarrow SD + CD_{3}$ reaction has been studied in a photolysis-probe experiment. $S(^{1}D)$ reagent was prepared by laser photolysis of CS_{2} , and the $SD(X^{2}\Pi)$ product was detected by laser fluorescence excitation. The nascent rotational/fine-structure state distribution of the $SD(X^{2}\Pi)$ product was determined. The experimentally determined rotational state distribution within each fine-structure manifold agrees well with the predictions of a statistical 'prior' distribution, while the F_{1} to F_{2} fine-structure branching ratio is higher than predicted statistically. The product state distribution is consistent with reaction through the formation and decay of an energized CD₃SD complex.

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1. Introduction

The dynamics of reactions of $O(^{1}D)$ atoms with hydrocarbons have been extensively studied, in part because of their importance in atmospheric chemistry. The most important of these reactions is $O(^{1}D) + CH_{4}$. This reaction has been studied by both laser fluorescence and infrared chemiluminescence detection of the products and in a crossed beam study [1–6]. As with many $O(^{1}D)$ reactions, this reaction proceeds through insertion to form an energized intermediate, which decays to products, with some memory of the initial preparation of the complex [5,6]. The dominant chemical pathway of the $O(^{1}D) + CH_{4}$ reaction is formation of $OH + CH_{3}$ products.

By contrast, the corresponding reactions of the $S(^{1}D)$ atom have been very little studied, and only in kinetic measurements. A critical evaluation of kinetic data [7] recommends a room-temperature rate constant of $\geq 5 \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹ for the $S(^{1}D) + CH_{4}$ reaction. A significant factor which has impeded state-

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resolved dynamical studies of reactions involving SH products is the rapid predissociation of $SH(A^2\Sigma^+)$ [8,9], which renders laser fluorescence detection of this radical problematic. Wittig and co-workers [10,11] investigated the dynamics of the reaction of D atoms with OCS in bimolecular collisions and within a van der Waals complex. In recent work, we have determined the rotational/fine-structure state distribution of SD products from the S(¹D) + D₂ reaction [12], to provide information complementary to that from crossed beam studies [13,14] and theoretical treatments of the dynamics [15–17] of this reaction.

In this Letter, we investigate the dynamics of the $S(^{1}D) + CH_{4}$ reaction. As in the $O(^{1}D) + CH_{4}$ reaction, several chemical exothermic pathways are possible:

$$S(^{1}D) + CH_{4} \rightarrow SH + CH_{4},$$

$$\Delta H_{0}^{o} = -26.7 \pm 0.8 \text{ kJ mol}^{-1},$$

$$\rightarrow H_{2}CS + H_{2},$$
(1a)

$$\Delta H_0^{\rm o} = -200 \pm 8 \text{ kJ mol}^{-1}.$$
 (1b)

The quoted reaction exothermicities were computed from available heats of formation and the S atomic excitation energy [18–21]. It should also be noted that

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formation of CH₃SH from S(¹D) + CH₄ is exothermic by 330.9 \pm 0.4 kJ mol⁻¹. In the O(¹D) + CH₄ reaction, several other exothermic channels are available, involving formation of H and H₂, but the OH + CH₃ pathway dominates (branching ratio determined to be 77% [6]). Similarly, we expect pathway Eq. (1a) to be dominant in the S(¹D) + CH₄ reaction.

Laser fluorescence excitation is employed here for the determination of the rotational/fine-structure state distribution of the SD product from the $S(^{1}D) + CD_{4}$ isotopic analog of reaction Eq. (1a) $[\Delta H_{0}^{o} = -22.2 \text{ kJ mol}^{-1}]$, using the SD $A^{2}\Sigma^{+} - X^{2}\Pi$ electronic transition [22]. The deuterated version of reaction Eq. (1a) has been studied because the excited-state predissociation is sufficiently slow in the deuterated isotopomer [8,9] that SD laser fluorescence excitation spectra with good signal-to-noise ratio could be recorded.

2. Experimental

This study was carried out in the same apparatus employed in our recent study [12] of the $S(^{1}D) + D_{2}$ reaction and has been described in detail previously [12,23,24]. A brief description of the experiment is presented here. The $S(^{1}D)$ reagent was prepared by 193 nm photolysis of CS_{2} (1 mTorr) in a quasi-static cell. The CD_{4} reagent (200 mTorr) and argon (300 mTorr, to retard deposition of sulfur on the windows) were introduced through the ends of the sidearms, and the gas mixture was flowed slowly through the cell. The excimer photolysis laser (Lambda Physik COMPex 102) and probe laser (frequency-doubled signal output of a Continuum Sunlite EX optical parametric oscillator) radiation were counterpropagated through sidearms on the cell.

Laser fluorescence excitation spectra were recorded in order to determine the internal state distribution of the SD reaction product. The SD fluorescence was detected with a photomultiplier/gated-integrator combination through a 1 m spectrometer operated at a resolution of 255 cm^{-1} . To minimize the effect of predissociation in the SD(A² Σ^+) state, the width of the integrator gate was set to detect only a small portion (30 ns, delayed 30 ns after the probe laser pulse) of the fluorescence decay profile [12]. Spectra were recorded with probe laser pulse energies of 0.25 mJ in a 0.35 cm diam beam. Previous work [12] indicated that these conditions were within the linear excitation regime.

3. Results

The total energy available to the products is the sum of ΔH_0° and the internal and translational energies of the reagents. The average rotational and vibrational ener-

gies of the room-temperature CD₄ reagent are 3.7 and 0.4 kJ mol^{-1} , respectively, and the internal excitation of the $S(^{1}D)$ reagent has already been taken into account in the computation of the exothermicity for the reaction. The average relative translational energy (19.8 kJ mol⁻¹) was obtained from the relative translational energy distribution calculated [12] by convolution of the velocity of the $S(^{1}D)$ fragment from 193 nm photolysis of CS₂ with an isotropic Maxwellian velocity distribution of the CD₄ reagent. Because of the greater mass of CD₄ vs. D₂, the velocity of $S(^{1}D)$ is more efficiently converted into relative translational energy of the reagents than in the $S(^{1}D) + D_{2}$ reaction. The total energy available to the $SD + CD_3$ products of the $S(^{1}D) + CD_{4}$ reaction is thus 46.1 kJ mol⁻¹. This energy is sufficient to allow formation of SD products in the v = 0 and 1 vibrational levels. Within v = 0, rotational levels as high as J = 27.5 and 25.5 within the F_1 $(\Omega = 3/2)$ and F_2 ($\Omega = 1/2$) manifolds, respectively, can be populated.

Laser fluorescence excitation spectra of the SD $A^2\Sigma^+ - X^2\Pi$ (0,0) band, with observation of emission in the (0,1) band, were recorded in order to determine the rotational/fine-structure state distribution of the SD($X^2\Pi$, v = 0) product of the S(1D) + CD₄ reaction. Excitation spectra were taken as a function of the delay between the photolysis and probe lasers. The excitation spectra at the shortest delays (200 and 350 ns) were quite similar, and the spectra at 200 ns were employed to compute the nascent SD internal state distribution. We also searched for the presence of SD($X^2\Pi$, v = 1) product by scanning through the (0,1) band, with detection of emission in the (0,0) band. We were not able to detect vibrationally excited SD products.

The relative intensities of the resolved SD lines were converted to populations with the help of fluorescence excitation line strength factors [25], assuming isotropic M_J distributions. We also took into account the fact that the spectrometer transmitted only a portion of the detected SD $A^2\Sigma^+ - X^2\Pi$ (0,1) emission band, namely near the R_1 head. Fluorescence excitation factors were calculated with inclusion of the spectrometer transmission factor for all the emission lines associated with each transition in the fluorescence excitation spectrum. For most of the SD rotational/fine-structure levels, it was possible to obtain redundant values of the populations from the intensities of different lines originating from the same level, while in some cases spectral congestion prevented determination of the relative populations from all the allowed lines. The populations were determined from averages of the populations from different resolved excitation lines.

The detection sensitivity for the individual levels is also affected by the increasing predissociation rate of the SD($A^2\Sigma^+$) excited levels as a function of N' [8,9]. The use of a short integrator gate mitigates the effect of the varying excited-state predissociation rate on the relative detection sensitivity of different levels, and a correction for the effect of predissociation has been applied to the measured intensities [12]. This correction becomes increasingly large with increasing N', as discussed previously [12].

Fig. 1 presents the derived relative populations of the rotational fine-structure levels of the SD($X^2\Pi$) product from the S(¹D) + D₂ reaction. The rotational state distribution within each fine-structure manifold is fairly broad, and the populations peak around $J \approx 10.5$. A significant preference for formation of the lower, F_1 fine-structure manifold can be observed. Summing over all observed rotational levels, the ratio of the population in the F_1 to F_2 manifolds is found to be 3.23 ± 0.13 .

The populations of the Λ doublet levels of A' and A" symmetry [26], in the high-*J* limit, are separately plotted in the two panels of Fig. 1. It can be seen that the populations of the Λ doublet levels of A' and A" symmetry for the same fine-structure manifold and rotational angular momentum are essentially the same. The ratios of the population of A' to A" levels, summed over all observed rotational levels, are computed to equal 1.11 ± 0.06 and 0.92 ± 0.08 in the F_1 and F_2 manifolds, respectively.



Fig. 1. The derived rotation fine structure state distribution of $SD(X^2\Pi, v = 0)$ products from the reaction of $S(^1D)$ with CD_4 . Upper panel: F_1 ($\Omega = 3/2$) fine-structure manifold; lower panel: F_2 ($\Omega = 1/2$) fine-structure manifold. The distributions have been normalized so that the sum of the populations in the v = 0 vibrational level is unity.

4. Discussion

The present study reports the internal state distribution of the SD(X²Π) product from the reaction of S(¹D) with CD₄, in particular the branching into the spin–orbit and Λ doublet levels. Because of the presence of the deeply bound CD₃SD well, which can be accessed from the reagents, this reaction should occur by insertion dynamics, involving the formation and decay of a collision complex. It is thus interesting to compare our experimentally determined rotational state distribution with a prediction from statistical theory. We compare in Fig. 2 the measured state distribution with the socalled 'prior' distribution [27]:

$$\sigma(v, J, F_i) = \sum_{v_1 v_2 v_3 v_4 J_C K_C} \sigma(v, J, F_i; v_1 v_2 v_3 v_4, J_C, K_C), \quad (2)$$

where $\sigma(v, J, F_i; v_1v_2v_3v_4, J_C, K_C)$ is the correlated-product state-resolved prior cross-section:

$$\sigma(v,J,F_i;v_1v_2v_3v_4,J_C,K_C) \propto (2J+1)(2J_C+1)[E-\varepsilon(v,J,F_i;v_1v_2v_3v_4,J_C,K_C)]^{1/2}.$$
(3)

The sum over CD₃ internal states in Eq. (2) reflects the fact that we do not observe the CD₃ product and hence do not resolve its product states. In Eq. (3), *E* is the total energy available to the SD + CD₃ products, and $\varepsilon(v, J, F_i; v_1v_2v_3v_4, J_C, K_C)$ is the internal energy of the correlated pair of SD and CD₃ product states. Since their energies are essentially identical, the SD(X²Π) A doublet levels associated with a given *J* and fine-structure manifold are predicted to have equal populations.

We see in Fig. 2 that the shape of the experimentally determined relative populations within a given finestructure manifold (F_1 or F_2) is well reproduced by a



Fig. 2. Comparison of the experimentally determined product $SD(X^2\Pi, v = 0)$ rotational fine-structure state distribution (symbols) with a prior statistical distribution (solid lines). The latter has been scaled so that the distribution in the F_1 fine-structure manifold matches the experimental distribution.

statistical distribution. This good agreement of the experimental and prior state distributions is consistent with formation and decay of an energized CD_3SD complex in the dynamics of the $S(^1D) + CD_4$ reaction.

While there is sufficient energy to populate SD rotational levels up to J = 25.5-27.5, the experimental and statistical rotational state distributions peak at much lower values of J. It is also interesting to note that the degree of rotational excitation of the SD product from the $S(^{1}D) + CD_{4}$ reaction is much less than that for the SD product of the $S(^{1}D) + D_{2}$ reaction [12], despite the fact that both reactions proceed by formation and decay of an energized complex and the energy available to the former reaction is significantly greater than for the latter. This reflects the approximately statistical partitioning of the available energy into the SD and CD_{3} internal degrees of freedom.

We observe in Fig. 2 that a slight preference for formation of the lower-energy F_1 fine-structure manifold over that for the F_2 manifold is predicted in the prior distribution. The ratio of the total populations in the F_1 to F_2 manifolds is computed for the prior distribution to equal 1.64. The slightly unequal populations result from the slightly greater energy available to relative translational energy and CD₃ internal energy in the case of SD products formed in the F_1 manifold, and resulting larger density of available states, than for products formed in the F_2 manifold. Our experimentally determined SD(X²\Pi) internal state distribution displays an even greater propensity for formation of products in the F_1 manifold. As noted above, we determine the fine-structure branching ratio to equal 3.23 ± 0.13.

This fine-structure propensity contrasts with the lack of such a propensity in the isoelectronic $O(^{1}D) + CH_{4}$ reaction [1,2]. The exothermicity of this reaction $(\Delta H_{0}^{\circ} = -191.3 \pm 1.2 \text{ kJ mol}^{-1})$ is much greater than that of the $S(^{1}D) + CH_{4}$ reaction. Moreover, the spinorbit constant *A* for OH(X²\Pi) is much less than for SH(X²\Pi) (A = -139 and -377 cm^{-1} , respectively [28]). Thus, the fine-structure splitting is a much smaller fraction of the total energy available to the products of $O(^{1}D) + CH_{4}$ than for $S(^{1}D) + CH_{4}$. The observed enhancement of the production of SD in the lower, F_{1} fine-structure manifold over that predicted by the prior distribution could be the result of a tendency of the energized CD₃SD complex to dissociate adiabatically to the lowest fine-structure state.

The populations of the Λ doublet levels associated with a particular rotational angular momentum J and fine-structure manifold of the SD(X²Π) product from the S(¹D) + CD₄ reaction have been found to have essentially equal populations. This observation contrasts with the Λ doublet propensities observed [1,2] in the OH(X²Π) product of the O(¹D) + CH₄ reaction. One very significant difference between the SD(X²Π) and OH(X²Π) states is the magnitude of the ratio of the spin–orbit constant A and the rotational constant B(A/B = -7.5 and -76.9, respectively [22,28]). The small value of this ratio for OH(X²Π) implies that this state approaches the Hund's case (b) limit at fairly low values of J. Within the case (b) limit, the Λ doublet levels can display different symmetries of the electronic wave function with respect to the plane of molecular rotation, and collisional Λ doublet propensities can be anticipated [29]. By contrast, SD(X²Π) remains near the Hund's case (a) limit for all rotational levels energetically accessible in the S(¹D) + CD₄ reaction.

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