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G. Nan, D. W. Neyer, P. L. Houston, and I. Burak

Citation: The Journal of Chemical Physics **98**, 4603 (1993); doi: 10.1063/1.464988 View online: http://dx.doi.org/10.1063/1.464988 View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/98/6?ver=pdfcov Published by the AIP Publishing

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## Electronic-to-vibrational, -rotational, and -translational energy transfer: $S(^{1}D) + CO$ , N<sub>2</sub>, O<sub>2</sub>, and CO<sub>2</sub> measured by Doppler spectroscopy

G. Nan, D. W. Neyer, and P. L. Houston

Department of Chemistry, Cornell University, Ithaca, New York 14853-1301

I. Burak

School of Chemistry, Tel Aviv University, Tel Aviv, Israel

(Received 23 October 1992; accepted 11 December 1992)

Collisions of  $S(^{1}D)$  with CO,  $N_{2}$ ,  $O_{2}$ , and CO<sub>2</sub> have been investigated to estimate the fraction of the sulfur electronic energy that is deposited in the internal degrees of freedom in the collision partner during the quenching of  $S(^{1}D)$  to  $S(^{3}P)$ . The experiment measures the Doppler profile of the  $S(^{3}P)$  product, a profile that depends both on the amount of energy disposed into the internal degrees of freedom and on the differential scattering cross section for the inelastic collision. For CO and  $N_{2}$  the results are consistent with a collision complex model for which the scattering is assumed to be isotropic in the collision plane and for which the energy is partitioned statistically into the degrees of freedom. Under the assumption of isotropic scattering, the results suggest that less energy than the statistical prediction is partitioned into translation for collisions with  $O_{2}$ , whereas more energy is partitioned into translation for  $CO_{2}$ .

#### **I. INTRODUCTION**

The study of energy transfer processes represents an important branch of physical chemistry, and considerable interest has focused on the quenching of electronically excited atoms.<sup>1</sup> However, most of the experimental studies thus far have examined only the decay kinetics of excited atoms with the aim of obtaining total quenching cross sections. A full understanding of the process requires measurements both of differential cross sections and of the partitioning of energy into final degrees of freedom.

The studies reported here explore spin forbidden energy transfer processes, a typical example of which might be the efficient quenching of the excited oxygen state  $O(^{1}D)$  by molecular species such as  $N_{2}$  or CO. In this process the  ${}^{1}D$  excited state of atomic oxygen is quenched collisionally to the <sup>3</sup>P ground state. Despite the large ( $\approx 2$ eV) energy difference and the weak spin orbital coupling, large quenching cross sections have been reported.<sup>2</sup> These observations have been interpreted as the result of formation of a N<sub>2</sub>O or CO<sub>2</sub> collision complex on the lowest singlet potential surface. The intersection region between the singlet [e.g.,  $O(^{1}D) + N_{2}$ ] and the triplet  $[O(^{3}P) + N_{2}]$ potential surfaces is crossed many times during the lifetime of the complex,<sup>3,4</sup> so quenching proceeds efficiently even though the spin-orbit interaction is weak. Classical trajectory calculations on two model potential surfaces demonstrated<sup>3</sup> that the complex formation is mainly a result of rotation excitation at low collision energies (0.03 eV), while at higher collision energies (1.2 eV) vibration excitation becomes more important. Also, at 1.2 eV collision energy the contribution from "direct" quenching, i.e., quenching in the absence of collision complex formation, becomes appreciable and accounts for half of the total quenching cross section.

The objective of the work reported here was to study the spin forbidden relaxation of the sulfur atom in the excited <sup>1</sup>D state. Quenching rates of  $S(^{1}D)$  by several molecular collision partners have been reported by Black and Jusinski and by our own group.<sup>5,6</sup> As in the case of  $O(^1D)$ , high cross section were found for molecular species like CO, CO<sub>2</sub>, N<sub>2</sub>, and O<sub>2</sub>, but neither the angular distribution of the products nor the partitioning of energy into the products has been measured previously. It is possible to obtain information on the energy partitioning between translational and internal degrees of freedom and on the angular distribution in the E-V,R,T transfer process from an analysis of the Doppler profiles of the products. In the experiments reported here we use the Doppler spectroscopic technique to measure the velocity of both the  $S({}^{3}P_{2})$ product and the  $S(^{1}D)$  precursor. The goal is to infer from these results the redistribution of the relaxation energy between the collision partners.

The methodology of the experiment is as follows.  $S(^{1}D)$  sulfur atoms are produced via the photodissociation of OCS at 222 nm and are then relaxed by the quencher Q into the  $S(^{3}P_{2})$  state. The two processes involved are

$$OCS \xrightarrow{222 \text{ nm}} CO + S(^{1}D) \quad \Delta E = -10 \text{ 640 cm}^{-1}, \quad (1)$$

$$S(^{1}D) + Q \rightarrow S(^{3}P_{2}) + Q \quad \Delta E = -9240 \text{ cm}^{-1}.$$
 (2)

About 50% of the available energy in process (1) appears as relative translational energy between the CO and  $S(^{1}D)$ fragments. Doppler profiles of the nascent  $S(^{1}D)$  enable us to obtain the distribution of relative velocity vectors in the *Q*-S center-of-mass frame. Doppler profiles of the  $S(^{3}P_{2})$ provide the laboratory-frame velocity distribution of the electronically relaxed product. The  $S(^{3}P_{2})$  distribution is related to the  $S(^{1}D)$  distribution through the distribution of scattering angles (the differential cross section) and through the distribution of energy in the final degrees of freedom. An estimation of the allocation of the 9240 cm<sup>-1</sup> relaxation energy of process (2) between the internal and translational degrees of freedom of the products is made by assuming limiting angular distributions and performing a Monte Carlo integration to fit the  $S({}^{3}P_{2})$  Doppler profile to an energy distribution. The results for CO and N<sub>2</sub> are consistent with the complex mechanism proposed by Tully<sup>4</sup> and Zahr *et al.*<sup>3</sup> for quenching of  $O({}^{1}D)$  by N<sub>2</sub>.

#### **II. EXPERIMENT**

 $S(^{1}D)$  was generated by photodissociation of OCS at 222 nm, while the velocity distributions of both  $S(^{1}D)$  and ground state  $S({}^{3}P_{2})$  were monitored through their Doppler profiles measured by laser-induced fluorescence (LIF). The experimental setup has been described in a previous paper.<sup>8</sup> Briefly, dilute mixtures of OCS in a variety of quenching partners were introduced into a glass cell<sup>6</sup> at a total pressure low enough such that the average number of collisions between the time of  $S(^{1}D)$  creation and the time of  $S({}^{3}P_{2})$  detection was <1. Thus, while the probability of  $S(^{1}D)$  relaxation on this time scale is small, so is the probability of secondary collisions which might disturb the nascent  $S({}^{3}P_{2})$  velocity distribution. That the experiment can be performed at all is due to the extremely high detection sensitivity. The pulsed photolysis light at 222 nm (3-4 mJ/pulse, 6 ns pulse length) was provided by a Nd:YAGpumped dye system (Quanta-Ray, DCR-2A with PDL-2 dye laser and WEX-1) using summing of the doubled dye laser output with the 1.064  $\mu$ m Nd:YAG fundamental. The polarization of the photolysis light could be varied with a double Fresnel rhomb (Karl Lambrecht). The vacuum ultraviolet (VUV) probe laser light, which propagated in a direction orthogonal to the photolysis laser, was generated by four-wave sum mixing in magnesium vapor,<sup>7</sup> where the two dye lasers (Lamda Physik FL2002E) were each equipped with an intracavity étalon and were pumped simultaneously by the same XeCl laser (Lamda Physik LPX200). To probe the  $S({}^{3}P_{2})$  velocity distribution, the VUV light with full-width at half-maximum (FWHM) 0.14 cm<sup>-1</sup> was scanned through the  ${}^{3}D_{3}^{0} \leftarrow {}^{3}P_{2}$  transition of sulfur at 67 843 cm<sup>-1</sup>, while to probe the  $S(^{1}D)$  the light was scanned through the  ${}^{1}P_{1}^{0} \leftarrow {}^{1}D_{2}$  transition at 69 051 cm<sup>-1</sup>. The LIF signal was monitored with a solar-blind photomultiplier (EMR 542G-09-17), averaged in boxcar integrator (Stanford SRS-250), and normalized by the VUV laser intensity. Timing was controlled by a digital delay/pulse generator (SRS DG 535) operating at a master frequency of 10 Hz.



FIG. 1. Doppler profiles of the  $S(^{1}D)$  produced in the photodissociation of 5 mTorr of OCS shown with the electric vector of the photolysis laser parallel (a) or perpendicular (b) to the propagation direction of the probe laser. The data are the open circles, while the solid line is a fitting function described in the text.

OCS was obtained from Matheson and further purified by freeze-pump-thaw cycles. CO,  $N_2$ ,  $O_2$ , and  $CO_2$  were purchased from Matheson. The pressure was measured with one of two capacitance manometers (MKS310, MKS221).

#### **III. RESULTS AND ANALYSIS**

The nascent Doppler profiles of the  $S(^1D)$  photolysis product, obtained from a low pressure OCS sample, are shown in Fig. 1 and are consistent with earlier studies of the photochemistry of OCS.<sup>7,8</sup> Figure 1(a) shows the Doppler profile obtained when the direction of probe beam propagation is parallel to the polarization vector of the photolysis beam, while Fig. 1(b) shows the profile obtained when the direction is perpendicular. The Doppler curves (open circles) are fit with a velocity distribution function (VDF, solid line) formed from a shifted Gaussian,

$$VDF(v,\theta) = \begin{cases} [1+\beta P_2(\cos\theta)](v-vs)^2 \exp[-m_{ocs}(v-vs)^2/(2RT_{loc})], & v \ge vs \\ 0, & 0 < v < vs \end{cases}$$
(3)

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FIG. 2. Doppler profiles of  $S({}^{3}P_{2})$  following photolysis of a mixture of 5 mTorr of OCS and 55 mTorr of CO as a function of the delay time between the photolysis and probe pulses.

where v and  $\theta$  are the speed and the angle relative to the polarization vector of the photolysis beam, respectively,  $m_{ocs}$  is the OCS mass, R is the gas constant,  $P_2(\cos \theta)$  is the second Legendre polynomial,  $v_s = 600$  m/s,  $T_{loc} = 1100$  K, and  $\beta = 0.5$ .

Doppler profiles of the  $S({}^{3}P_{2})$  species were measured for OCS-quencher gas mixtures. The experiments were per-



FIG. 3. Relaxation of  $S(^{1}D)$  by CO. Comparison of the measured (open circles) and the calculated (solid lines) Doppler profiles for  $S(^{3}P_{2})$  Doppler profiles assuming either a collision complex model with f=0.40 (middle panel) or a direct model with forward (top panel) or backward (bottom panel) scattering and f=0.10 or 0.70, respectively.



FIG. 4. Relaxation of  $S(^{1}D)$  by N<sub>2</sub>. Comparison of the measured (open circles) and the calculated (solid lines) Doppler profiles for  $S(^{3}P_{2})$  Doppler profiles assuming either a collision complex model with f=0.47 (middle panel) or a direct model with forward (top panel) or backward (bottom panel) scattering and f=0.15 or 0.70, respectively.

formed for different time delays between the 222 nm dissociating pulse and the VUV probe pulse. Figure 2 displays the various profiles obtained from a mixture of 5 mTorr of OCS and 55 mTorr of CO at different time delays. The Doppler profile curves grow in intensity with increasing time delay between the 222 nm photolysis pulse and the VUV probe pulse. The Doppler profiles due to the collisionally induced singlet-triplet quenching are obtained by subtraction of the contribution due to the directly produced  $S({}^{3}P_{2})$  species.

Special care has been taken to ensure that the measured Doppler profiles represent the result of "one collision" between the sulfur atom and the quenching gas. The partial pressures of the OCS and quencher gases,  $P_{\rm ocs}$  and  $P_{\rm quencher}$ , respectively, were adjusted to fulfill the following condition:

$$k_{\rm ocs} P_{\rm ocs} t \ll k_{\rm quencher} P_{\rm quencher} t \ll 1, \tag{4}$$

where  $k_i$  is the S(<sup>1</sup>D) quenching rate constant due to a collision with the *i*th species and *t* is the time delay between the photolysis and the VUV pulses. Data concerning singlet-triplet relaxation rates constants,  $k_i$  for different quenchers were taken from Ref. 5. Finally, the subtracted Doppler profiles were checked and found to scale linearly with the delay time *t* up to delays of 450 ns. The subtracted Doppler curves for the different species are shown as the open circles in the panels of Figs. 3–6, where the polarization vector of the dissociation laser was parallel to the propagation direction of the probe beam. In contrast to the



FIG. 5. Relaxation of  $S(^{1}D)$  by  $O_{2}$ . Comparison of the measured (open circles) and the calculated (solid lines) Doppler profiles for  $S(^{3}P_{2})$  Doppler profiles assuming either a collision complex model with f=0.35 (middle panel) or a direct model with forward (top panel) or backward (bottom panel) scattering and f=0.05 or 0.50, respectively.

 $S(^{1}D)$  profiles, very little change is observed when the polarization is turned into a perpendicular configuration, as shown for CO and N<sub>2</sub> quenching in Fig. 7.

The goal of the analysis is to determine the average fraction f of the available energy which appears in the translation degrees of freedom of the  $S({}^{3}P)$  and its collision partner after E-V,R,T transfer from  $S({}^{1}D)$ . The fraction 1-f is then the average fraction of the available energy allotted to the internal degrees of freedom of the collision partner.

 $S({}^{1}D)$  produced from 222 nm photolysis of roomtemperature OCS has an average speed of 1280 m/s and an effective anisotropy parameter  $\beta = 0.5$ .<sup>8</sup> The initial collision energy  $\langle E \rangle_{col}^{0}$  depends on the mean relative velocity and the reduced mass and is 0.14, 0.14, 0.15, and 0.17 eV for collisions with CO, N<sub>2</sub>, O<sub>2</sub>, and CO<sub>2</sub>, respectively. The electronic transition energy between  $S({}^{1}D)$  and the ground triplet state  $S({}^{3}P_{2})$  is  $E_{ex}=1.145$  eV. Thus,  $\langle E \rangle_{av}=E_{ex}$  $+\langle E \rangle_{col}^{0}\approx 1.3$  eV of energy is available for partitioning among the relative translation and the vibrational and rotational degrees of freedom of the collision partner,

$$E_{\rm ex} + E_{\rm col}^0 = \Delta E_{\rm vibrot} + E_{\rm tr},\tag{5}$$

where  $E_{\rm tr}$  is the relative translational energy after the energy transfer collision. The average fraction f of the available energy allocated to translation is then

$$f = \langle E_{\rm tr} \rangle / \langle E_{\rm av} \rangle, \tag{6}$$



FIG. 6. Relaxation of  $S({}^{1}D)$  by CO<sub>2</sub>. Comparison of the measured (open circles) and the calculated (solid lines) Doppler profiles for  $S({}^{3}P_{2})$  Doppler profiles assuming either a collision complex model with f=0.50 (middle panel) or a direct model with forward (top panel) or backward (bottom panel) scattering and f=0.25 or 0.70, respectively.



FIG. 7. Comparison of  $S({}^{3}P_{2})$  Doppler profiles taken with the electric vector of the photolysis laser parallel (solid lines) or perpendicular (dashed lines) to the propagation direction of the probe laser following quenching of  $S({}^{1}D)$  by (a) CO and (b) N<sub>2</sub>.

TABLE I. Comparison of the statistical fraction of energy in translation with the measured fraction.

Collision partner	$\langle V \rangle_{\rm rel}^0$ (m/s)	$\langle E \rangle_{\rm col}^0$ (cm <sup>-1</sup> )	$E_{\rm av}$ (cm <sup>-1</sup> )	$\langle E \rangle_{\rm tr}^{\rm prior}$ (cm <sup>-1</sup> )	f <sup>prior</sup>	fexpt a	$k (10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1})$
CO	1353	1143	10 382	4869	0.469	$0.40 \pm 0.05$	6.3 <sup>b</sup>
$N_2$	1353	1143	10 382	4903	0.472	$0.47 \pm 0.05$	8.5°
$O_2$	1345	1210	10 449	4770	0.456	$0.35 \pm 0.05$	5.3°
CO <sub>2</sub>	1329	1368	10 607	2995	0.282	$0.52 \pm 0.05$	15°

\*Assuming an isotropic scattering distribution.

<sup>b</sup>Taken from Ref. 10.

Taken from Ref. 5.

with the remainder going to the internal degrees of freedom in the quenching gas. Using the Doppler profiles of Figs. 3–6 and assuming that the differential scattering cross section is isotropic (center panels of each figure), we have determined the fractions f for the various collision partners shown in Table I. This table also presents a comparison of the experimental results with the results of a statistical prior distribution based on the available energy. The fraction of energy deposited into translation for the prior distribution is denoted  $f_{\rm tr}^{\rm prior}$  and is calculated as the ratio  $\langle E \rangle_{\rm tr}^{\rm prior}/E_{\rm av}$ , where  $\langle E \rangle_{\rm tr}^{\rm prior}$  is the average translation energy for the prior distribution.

The Doppler profile is actually dependent not only on the fraction of energy f deposited into translation but also on the differential scattering cross section. We now examine the effect of different differential scattering functions.

For the analysis described below, we make the simplifying assumption that the distribution of internal energy in the collision partner is characterized by a delta function centered about its first moment, 1-f of the available energy. We examine the effect of the width of the distribution later. Then, for an assumed differential scattering function, we calculate the expected Doppler profile by integration over the dynamical variables using a Monte Carlo technique, as described in detail elsewhere.<sup>8</sup> Briefly, the initial velocities for  $S(^{1}D)$  were sampled from the known velocity distribution produced in the dissociation of OCS, while initial velocities for the collision partner were sampled from a room temperature Boltzmann distribution. The initial velocities were then transformed into the center-ofmass (c.m.) frame, where a fraction f of the available energy is partitioned to the relative translation between the relaxed  $S({}^{3}P_{2})$  and the (internally excited) collision partner. The c.m. final velocities are calculated by sampling from an assumed differential scattering cross section, and the expected Doppler profiles are obtained by transforming the final c.m. velocities back to the laboratory frame and binning the component of velocity along the probe laser direction of propagation.

Several differential scattering functions were considered. One reasonable model for the E-V,R,T transfer is that the partners form a collision complex which lives for at least one rotational period before dissociating to products. A collision complex involving two structureless particles would be characterized by isotropic scattering in the plane of collision and an angular distribution  $I(\Theta) \propto (\sin \Theta)^{-1.9}$  For a collision complex involving molecules, the scattering is no longer necessarily confined to the collision plane, since the rotational angular momenta of the molecule can couple to the orbital angular momentum of the complex. However, if the complex is long-lived the scattering should still be symmetric about 90° in the c.m. frame.

An alternative models is that the E-V,R,T transfer takes place by a direct collision. Such a mechanism would not be characterized by symmetric scattering in the c.m. frame; either forward or backward scattering would be more likely.

One possible experimental distinction between the different differential scattering functions can be made by varying the direction of the polarization vector of the dissociating light relative to the propagation of the probe laser. In principle, the Doppler profiles measured under different geometries are characteristic of the differential scattering function. However, the differences are obscured by the collisional randomization of the initial anisotropy, so that for our experimental conditions the measured  $S({}^{3}P_{2})$  Doppler profiles should be sensitive to polarization only in the case of forward scattering. Thus, by changing the polarization of the photolysis laser, forward scattering can be distinguished from isotropic or backward scattering.

With f as a parameter, the  $S({}^{3}P_{2})$  Doppler profiles following a quenching collision were calculated for two polarization geometries and for (1) the collision complex model, where we assumed isotropic scattering in the collision plane with a  $(\sin \Theta^{-1})$  distribution, and (2) the direct model, where either (a) forward or (b) backward scattering is assumed with a  $(\sin \Theta)^{-1}$  distribution for the angular distribution on the corresponding hemisphere. The results are described below.

For collisions of  $S(^{1}D)$  with CO, N<sub>2</sub>, O<sub>2</sub>, and CO<sub>2</sub>, Figs. 3-6, respectively, compare the measured  $S(^{3}P_{2})$  Doppler profiles with the calculated profiles for the "parallel" polarization geometry and for isotropic (middle panel), forward (top panel), or backward scattering (bottom panel).

The parameter f for a delta function energy distribution has been varied in the calculation, and the best fits are shown in Figs. 3–6. In all of the four quenching molecules, CO and N<sub>2</sub> in particular, the line shape of the calculated Doppler profiles for forward or backward scattering is quite different from that measured; the measured speed

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FIG. 8. Calculated Doppler profiles for (a) forward scattering with f=0.10 and (b) isotropic scattering with f=0.40 for parallel and perpendicular polarization.

distribution is broader and the angular distribution is more isotropic than those calculated for the direct model. The line shape calculated for complex forming collisions is much closer to the measured one. The *f* parameters for this model are 0.40, 0.47, 0.35, and 0.52 for CO, N<sub>2</sub>, O<sub>2</sub>, and CO<sub>2</sub>, respectively, each with an uncertainty of  $\pm 0.05$ . In O<sub>2</sub>, the data are not completely consistent with the complex forming mechanism, since a calculated Doppler profile which sums contributions from both direct scattering and isotropic scattering gives a better fit to the measured profile than does the isotropic scattering itself.

The effect of the second moment of the distribution was investigated by assuming that the distribution of energy deposited into internal degrees of freedom was a Gaussian truncated at f=0 and 1, rather than a delta function. Even for FWHM values of  $1.6\langle E \rangle_{av}$ , the calculated Doppler profiles were insensitive to the width of the Gaussian distribution. We can thus conclude that while the experiment provides the average of the distribution function, it provides no information about its width (second moment).

#### **IV. DISCUSSION**

## A. CO and N<sub>2</sub>

For quenching of  $S({}^{1}D)$  with CO or  $N_{2}$ , the fraction of energy deposited in translation obtained from the Doppler profiles using the complex forming model is consistent with the fraction calculated from the statistical model to within the uncertainties of the experiment and the calculation. If a collision complex is formed on the singlet surface and if the intersection between the singlet  $[S(^{1}D) + CO, N_{2}]$  and the triplet  $[S(^{3}P_{2}) + CO, N_{2}]$  surfaces is passed many times during the lifetime of the complex, a statistical distribution of the available energy is to be expected.

The fact that the measured Doppler profiles give fits which agree with the statistical model lends support to a collision complex model, but it cannot be taken as proof. It is theoretically possible to match the observed Doppler profile using direct forward scattering, but only if a broad distribution is used for f, for example, one for CO having equal probabilities at the values for f=0.0, 0.1, 0.2, and0.3, rather than one centered sharply at f=0.40 as used in the case of isotropic scattering. The average energy disposed into translation would then be 0.15 and not in agreement with the statistical model. However, the possibility of forward scattering can be ruled out by the observation, shown in Fig. 7, that the  $S(^{3}P_{2})$  Doppler profile is insensitive to the polarization direction of the photolysis light. Figure 8 shows calculated Doppler profiles for (a) forward scattering with f=0.10 and (b) isotropic scattering with f=0.40 for parallel and perpendicular polarization. A marked difference is predicted for the two polarizations for the forward scattering, in contrast to what is observed in Fig. 7. For isotropic scattering, no such difference is predicted. Although forward scattering can be ruled out by our observations, backward scattering cannot. Thus, while our data are consistent with a collision complex model, they admit the possibility of a direct process with backward scattering. The direct and the complex mechanism are two extremes in the E-V, R, T transfer process. At low collision energies the complex model may be a dominant mechanism, while at higher collision energies the direct mechanism might play an important role.

Experimental confirmation of a complex forming model would not be surprising. The singlet initial surface and the triplet final state intersect at a location that determines the dynamics of the energy transfer. If the location of the intersection surface is too high in energy, the quenching process will be very inefficient, but if the intersection is accessible in energy, trajectories may cross the surface many times, leading to more efficient quenching. The quenching rate of  $S(^{1}D)$  by N<sub>2</sub> has been measured previously as  $8.5 \times 10^{-11}$  cm<sup>3</sup> molec<sup>-1</sup> s<sup>-1.5</sup> In a separate study, we have measured the quenching rate by CO to be  $6.3 \times 10^{-11}$  cm<sup>3</sup> molec<sup>-1</sup> s<sup>-1.10</sup> These rates correspond to a quenching event every 4–6 hard sphere collisions, so it is clear that the quenching is efficient.

Our conclusion that the energy partitioning between V, R, and T is consistent with a statistical model at first seems to contradict our previous measurement that the branching ratio of the three  ${}^{3}P_{j}$  components is not statistical for  $S({}^{1}D) + N_{2}$ .<sup>6</sup> However, these observations may be rationalized as follows: the intersection surface between the singlet and the three different triplet potential surfaces may be located at very different energies. One of the triplet intersections, for example, might be located at a higher energy than the others, so that vibrations of the collision

complex on the singlet surface do not access the intersection. Thus, the branching ratio to that triplet component might be smaller even though intersections of the singlet potential surface with the other triplet components are accessed many times by the collision complex and lead to statistical distribution of the products.

## B. O<sub>2</sub> and CO<sub>2</sub>

For O<sub>2</sub>, the assumption of a collision complex model (isotropic scattering) is best fit by  $f^{\text{complex}}=0.35$ , whereas the statistical prediction is  $f^{\text{prior}}=0.456$ . Although the difference between the model and experiment is not very large, another model assuming a summed contribution of the complex and the direct model with backward scattering gives a line shape closer to that of experimental measurement. It is possible that for this system the contribution of the direct mechanism is not negligible. A second possibility is that nearly resonant electronic transfer of the type  $S(^{1}D) + O_{2}(^{3}\Sigma) \rightarrow S(^{3}P) + O_{2}(^{1}\Delta)$  may be occurring. With the larger molecule CO<sub>2</sub>,  $f^{\text{complex}}=0.5$  differs

considerably from  $f^{\text{prior}} = 0.28$ . One expects that when the number of internal degrees of freedom increases in the quencher, the collision complex should become more stable, since the collision energy can be dissipated into more internal degrees of freedom. The cross section for complex formation should thus increase, and the rate of unimolecular dissociation of the complex should decrease. In Table I the total quenching rates for  $S(^{1}D)$  by CO<sub>2</sub>, N<sub>2</sub>, and O<sub>2</sub> measured by Black et al.<sup>5</sup> are also listed for reference. The total quenching rate by  $CO_2$  is indeed larger than that by  $N_2$  or  $O_2$ . It is somewhat surprising to find from our results that not all the internal degrees of freedom in CO<sub>2</sub> appear to participate in the quenching process. If the quenching takes place through formation of a collision complex, apparently the lifetime of the complex is not long enough for the energy to be dissipated statistically.

#### **V. CONCLUSION**

Doppler profiles of  $S({}^{3}P_{2})$  have been measured following the creation of  $S({}^{1}D)$  from OCS photolysis at 222 nm

and its subsequent relaxation due to single collisions with CO, N<sub>2</sub>, O<sub>2</sub>, and CO<sub>2</sub>. The profiles depend on both the differential cross section for the inelastic collision and on the distribution of energy partitioned into the internal degrees of freedom of the quenching molecule. For CO and  $N_2$  the results are consistent with a collision complex model for which the scattering is assumed to be isotropic in the collision plane and for which the energy is partitioned statistically into the internal degrees of freedom. The possibility of forward scattering can be ruled out because the Doppler profiles should be sensitive to the polarization geometry for such scattering, whereas the experiment shows the profiles to be independent of polarization. While backward scattering might still be possible, it appears that a collision complex mechanism is the most likely explanation for the CO and  $N_2$  results. The case is less clear for  $O_2$  and CO<sub>2</sub>, where less or more, respectively, energy is partitioned into translation than would be predicted from a long-lived collision complex.

#### ACKNOWLEDGMENT

This work was supported by the Air Force Office of Scientific Research under Grant No. F49620-92-0080.

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