QUENCHING OF ELECTRONICALLY EXCITED CS$_2$ (^{1}A$_2$ AND ^{3}A$_2$ STATES) BY SEVERAL COLLISION PARTNERS

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(Received October 23, 1981)

Summary

The lifetimes of electronically excited CS$_2$ were determined in the presence of selected quenchers. Cross sections for the collisional quenching of CS$_2$* by O$_2$, NO, CO$_2$, CH$_3$OH, C$_2$H$_5$OH, CCl$_4$ and C$_2$H$_5$NO$_2$ are reported. O$_2$ and C$_2$H$_5$NO$_2$ at high pressures give CS$_2$* lifetimes longer than those calculated from the low pressure rate constants.

A model for collision-induced transitions from one electronic state to a near continuum of vibronic levels of another electronic state of the same molecule was used to correlate the quenching cross sections to parameters which are characteristic of the quencher. The results show that the quenching of the singlet state is of the order of four times more efficient than that of the triplet.

1. Introduction

The transfer of a specific type of electronic excitation into other forms of electronic, vibrational, rotational and translational excitation as a result of intermolecular interaction is of paramount importance for the understanding of many photochemical and photophysical processes. It is also important for the understanding of many phenomena which occur in the atmosphere. The intensity of the spontaneous emission from a molecular state provides an accurate probe of the population of that state. Thus, by monitoring the luminescence from a given state as a function of time, the flow of energy into and out of that state can be determined.

The photochemistry and spectroscopy of CS$_2$ have been investigated by several groups in recent years [1 - 6]. The main reason for the interest in this molecule is that it is included in the group of molecules like NO$_2$ and SO$_2$ that show intermediate behaviour, *i.e.* CS$_2$ shows some characteristics of a molecule that undergoes radiationless transitions and some characteristics of a species that emits resonance radiation.

Since 1966, when Douglas [1] pointed out that the lifetimes reported for certain states of CS_2, NO_2 and SO_2 were significantly longer than those predicted from integrated absorption coefficients, there have been many investigations of the nature of the phenomena involved in the photochemistry of these molecules.

The laser-induced fluorescence technique has been used to show that fluorescence decay in the low pressure regime is not exponential but has short- and long-lived components [3 - 5]; at higher pressures only the long-lived component is present [7]. Frequency-resolved fluorescence spectra reveal both discrete and continuous features [3, 4]. Matsuzaki and Nagakura [4] have pointed out that the magnetic quenching of fluorescence is due to the enhancement of an intramolecular non-radiative process. Lester and Flynn [8] have recently demonstrated the existence of inverse relaxation in SO_2, which suggests that the relaxation phenomenon occurs with a high probability in this type of molecule. In previous work [9] we reported the existence of two different long-lived states in view of the detection of luminescence in the wavelength region centred at 5860 Å. The quenching of electronically excited CS_2 by other substances has been reported by Lambert and Kimbell [10].

In this paper we report investigations of the collisional quenching of electronic excitation in CS_2 using O_2, NO, CO_2, CH_3OH, C_2H_5OH, CCl_4 and $C_2H_5NO_2$ as collision partners. The emission was collected at two different wavelengths, 4480 and 5860 Å. We used a model developed by Thayer and Yardley [11] to correlate the quenching cross sections with characteristic parameters of the quenchers. This model is useful for collision-induced transitions from one electronic state to a near continuum of vibronic levels of another electronic state in the same molecule. The quenching efficiencies can also be related to current theories [12] which deal with the importance of collisions in radiationless transitions.

The laser excitation at 3371 Å is in the region of bands of the $T\ ^1A_2-X\ ^1\Sigma_g^+$ system. Other states are located near this state and interact with it. Jungen *et al.* [2] have studied the absorption spectrum near 3371 Å and have assigned the $^1A_2$ state and a triplet state as the two fluorescing states.

2. Experimental details

A nitrogen laser operating at a wavelength of 3371 Å with a pulse length of 10 ns and a power of 2 mJ pulse^{-1} was used.

The gases were handled in a standard glass vacuum line with a background pressure below 10^{-6} Torr and a leak rate of less than 2×10^{-6} Torr min^{-1}. A standard Pyrex fluorescence cell with the outside painted black to minimize light scattering was connected to the vacuum line. The CS_2 sample (Merck, at least 99.9% pure) was located in a Pyrex reservoir attached to the vacuum line. In order to attain a very low pressure, the reservoir was cooled

by liquid nitrogen and warmed up very slowly. The CS_2 sample was degassed several times prior to use.

The bottled gas quenching partners were of the highest purity available (at least 99.9%). To maintain the purity, each gas bottle was opened to the transfer line under a high vacuum. The liquid quenching partners were also of high purity (at least 99.9%) and were carefully degassed and vacuum distilled before use.

Pressures in the range 0.01 - 0.5 Torr were measured with a calibrated manometer (Pirani 6722) and pressures in the range 0.5 - 1 Torr were measured with a McLeod manometer. All the experiments were performed at room temperature.

The beam from the nitrogen laser was focused and collimated in order to minimize light scattering and to enhance the collected emission. Bandpass interference filters were used to isolate the fluorescence zone under investigation. Additional glass UV cut-off filters were inserted between the cell and the interference filter to reduce the scattered light intensity further.

The CS_2 fluorescence was detected with an AVP-56 photomultiplier. The signal from the photomultiplier was delayed by 1.8 μs with respect to the laser pulse to avoid electrical noise. It was then amplified and transmitted to a boxcar circuit where it was averaged over a sufficient number of pulses to obtain a good signal-to-noise ratio. The signal was simultaneously displayed visually on a Tektronix model 7704 oscilloscope.

3. Results

3.1. Experimental results

We studied the collisional quenching of electronically excited CS_2 by O_2, NO, CO_2, CH_3OH, C_2H_5OH, CCl_4 and $C_2H_5NO_2$. The fluorescence emission was observed in the spectral regions centred at 4480 and 5860 Å, and the lifetimes of the $^1A_2$ and $^3A_2$ states were measured as a function of pressure for all the quenching gases. The pressure of CS_2 was 0.01 Torr for all the quenching data reported in this work.

Table 1 shows the quenching rate constants and cross sections for the long- and short-lived components, and Figs. 1 - 5 show examples of the Stern–Volmer plots obtained. It should be noted that in all cases the highest pressure is that for which the signal-to-noise ratio is good enough for reliable data to be obtained; at higher pressures the emission intensity is too low.

The striking feature is the pronounced non-linear behaviour shown in Figs. 3 and 5 for quenching by O_2 and $C_2H_5NO_2$ at 4480 Å. The rate constants listed in Table 1 for these two quenchers were derived from the slopes of the low pressure linear regions.

3.2. Application of the model of Thayer and Yardley

Thayer and Yardley [11] have developed a theory of spin-allowed radiationless transitions induced by collisions. In this theory a collision

TABLE 1

Rate constants for the quenching of electronically excited CS_2 by various quenchers at 25 °C

| Collision partner	Rate constant (10^{-10} cm³ molecule⁻¹ s⁻¹)				Cross section (Å²)				Gas kinetic cross section (Å²)
	4480 Å		5860 Å		4480 Å		5860 Å		
	K_s	K_f	K_s	K_f	σ_s	σ_f	σ_s	σ_f	
O_2	0.79	2.92	0.53	2.48	15	55	10	47	49
$C_2H_5NO_2$	4.70	23.17	3.63	17.5	115	565	89	427	89
CO_2	0.96	3.26	0.81	2.72	20	68	17	57	56
NO	0.89	2.86	0.63	2.0	16	53	12	37	49
CH_3OH	3.57	15.53	2.69	12.7	67	292	51	239	51
CCl_4	0.98	3.62	0.82	2.85	28	102	23	80	84
C_2H_5OH	2.59	12.33	1.98	9.8	55	262	42	208	62
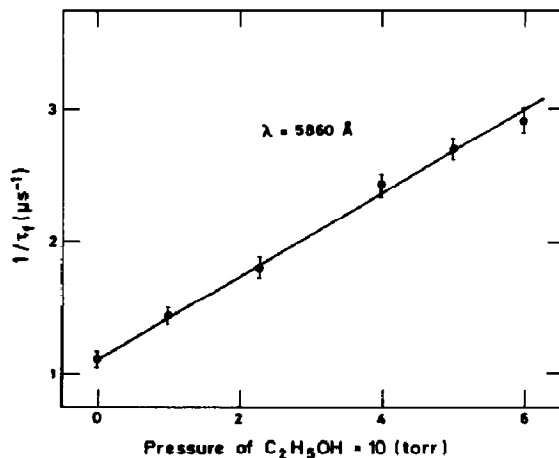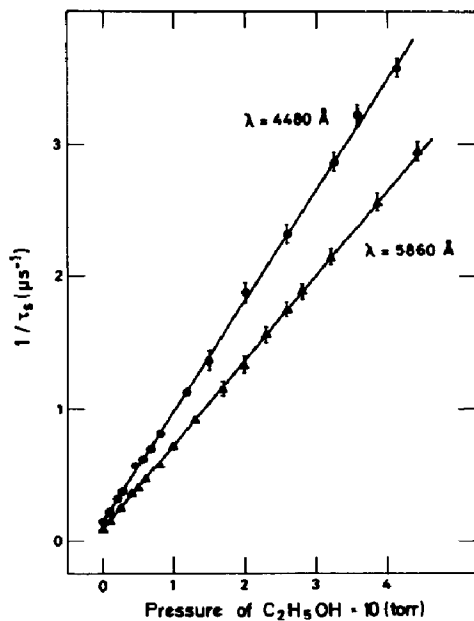
Fig. 1. Stern–Volmer plots for the quenching of the $^3A_2$ triplet state by C_2H_5OH at 4480 and 5860 Å.

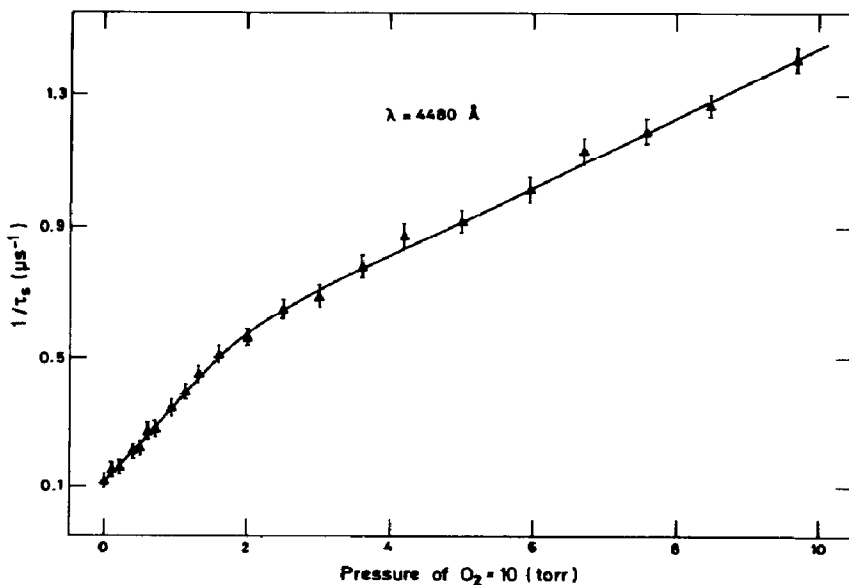Fig. 2. Stern–Volmer plot for the quenching of the short-lived component ($^1A_2$ state) by C_2H_5OH at 5860 Å.

Fig. 3. Stern–Volmer plot for the quenching of the long-lived component by O_2 at 4480 Å. The saturation effect also occurs at 5860 Å.
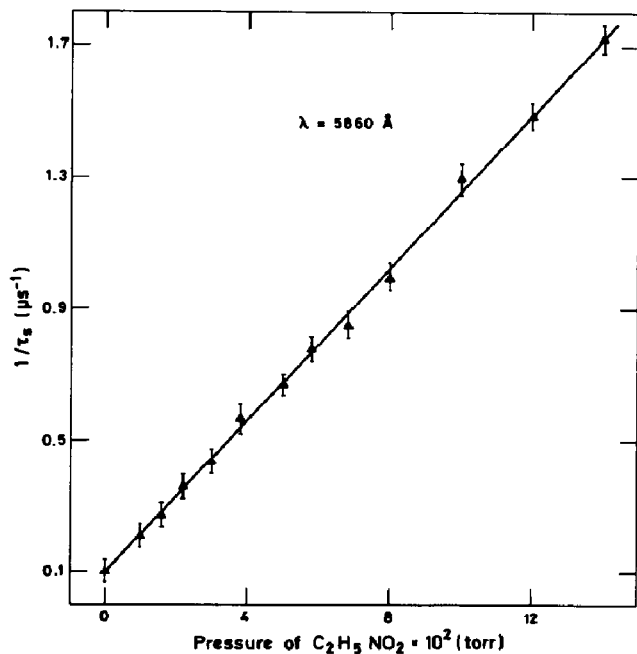
Fig. 4. Stern–Volmer plot for the quenching of the triplet state by $C_2H_5NO_2$ at 5860 Å.
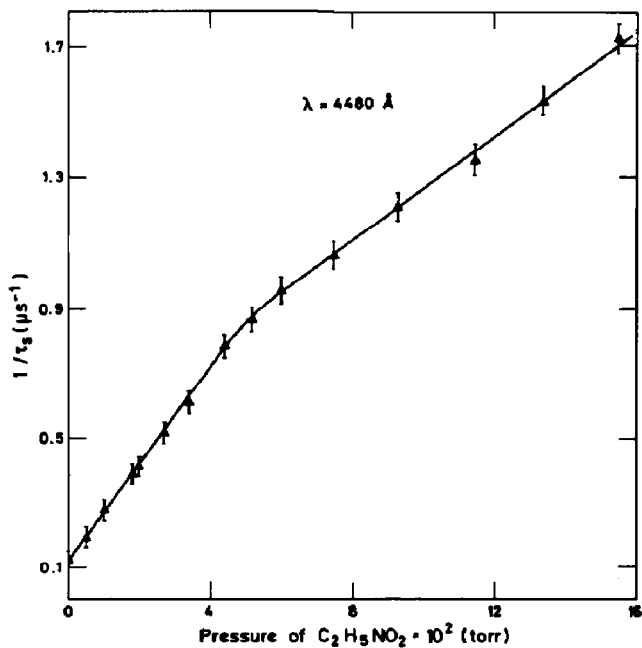

Fig. 5. Stern–Volmer plot for the quenching of the long-lived component by $C_2H_5NO_2$ at 4480 Å.

between an electronically excited molecule P and a polar or non-polar quenching partner Q is considered. The final result suggests that the variation in the quenching cross sections with the collision partner should be of the form

$$\sigma = AX + C \tag{1}$$

where

$$X = \mu^{1/2} I_P^2 I_Q^2 (I_P + I_Q)^{-2} \alpha_Q^2 R_c^{-9} \tag{2}$$

Here μ is the collisional reduced mass, I_P and I_Q are the ionization potentials of P and Q respectively, α_Q is the polarizability of the quencher and R_c is the Lennard-Jones collision diameter. A is a constant depending on the effective density of states ρ of the final state of the transition and other parameters.

The behaviour of quenching by polar partners is expected to obey the relation

$$\sigma = AX + BY + C \tag{3}$$

or

$$\sigma = A\mu^{1/2} I_P^2 I_Q^2 (I_P + I_Q)^{-2} \alpha_Q^2 R_c^{-9} + B\mu^{1/2} D_Q^2 R_c^{-3} + C \tag{4}$$

where D_Q is the dipole moment of the collision partner and B is an adjustable parameter.

Later, Thayer and Yardley [13] modified their theoretical model for spin-forbidden radiationless transitions induced by collisions and obtained an expression for the quenching cross section that differed from the previous result (eqn. (4)) by the factor

$$\frac{(D_P^{kf})^2}{(D_P^{if})^2} (S^{ik})^2 (E_i^0 - E_k^0)^{-2} \tag{5}$$

where i, k and f denote the initial, intermediate and final states respectively,

$$(D_P^{if})^2 = \sum_\beta (D_P^{if})_\beta^2$$

where $(D_P^{if})_\beta$ is a transition moment matrix element,

$$S^{ik} = \langle \Psi_i^s | H_{so} | \Psi_f^{s'} \rangle$$

where s and s' are the spin multiplicities of the electronic states, H_{so} is the intramolecular perturbation due to spin–orbit coupling and E_k^m is the energy of molecule P in the electronic state k and the vibrational state m. If the factor $(D_P^{kf})^2 (S^{ik})^2 (E_i^0 - E_k^0)^{-1}$ [13] is sufficiently small, the model developed previously by Thayer and Yardley [11] (see eqn. (4)) should be applicable to cases like glyoxal [14] and CS_2 where collisional deactivation of the singlet state results primarily in the formation of molecules in the corresponding triplet state.

We plotted σ as a function of the parameter X according to eqns. (2) and (4) for all the quenching gases including CS_2, the self-quenching data of
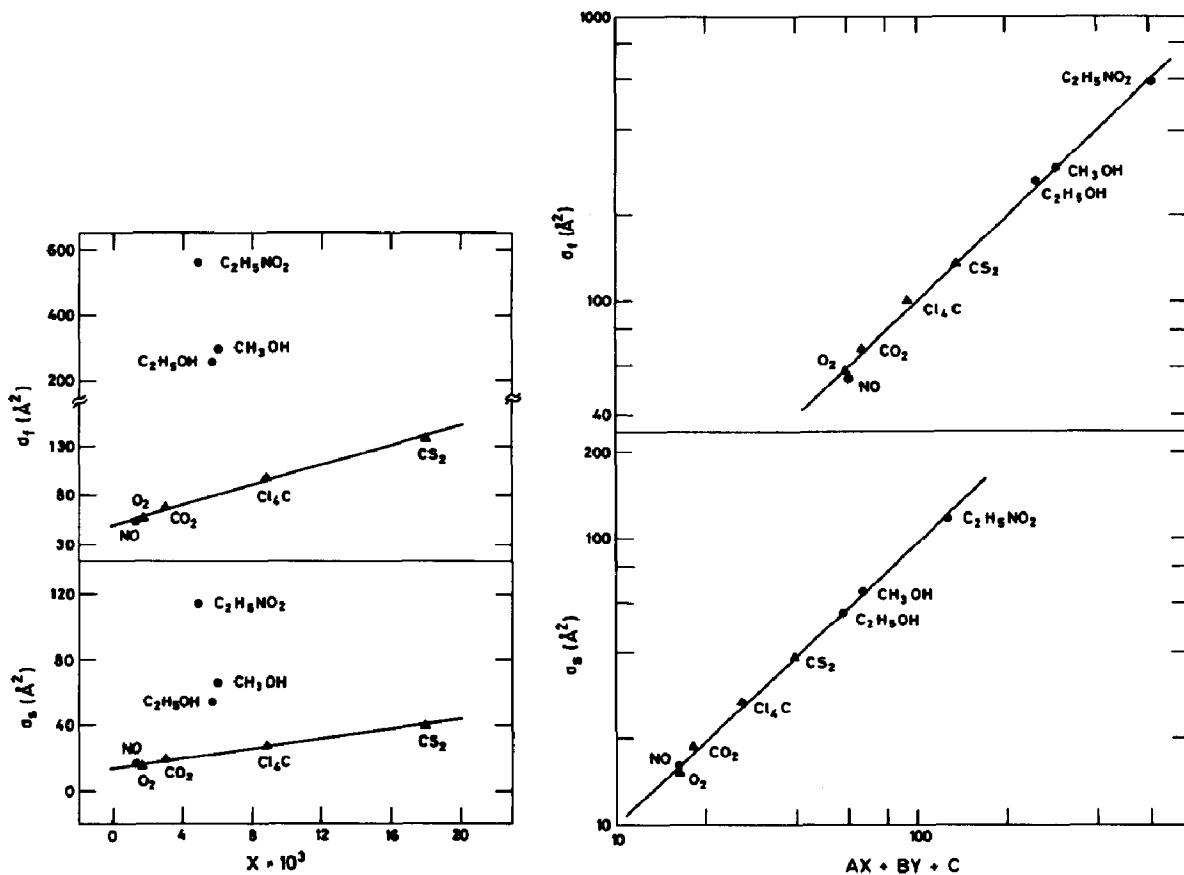
Fig. 6. The quenching cross sections for the $^3A_2$ and $^1A_2$ states *vs.* X for polar (●) and non-polar (▲) molecules. These results and those of Fig. 7 were obtained at 4480 Å; similar results were obtained for the emission at 5860 Å.

Fig. 7. The quenching cross sections for both components as a function of the Thayer and Yardley dispersion force parameter for polar (●) and non-polar (▲) quenchers.

which were taken from previous work [9]. The result can be seen in Fig. 6 where σ_f and σ_s are the cross sections for the fast and the slow components respectively and were obtained for the emission centred at 4480 Å. The use of eqn. (4) should allow correlation of the data for both polar and non-polar collision partners if the model is adequate.

Figure 7 shows plots of σ_f and σ_s as functions of $AX + BY + C$. The data given in Table 2 were used to calculate the X and Y parameters.

4. Discussion

Let us first examine the non-linear Stern–Volmer kinetics of the quenching of $CS_2(^3A_2)$ by O_2 and $C_2H_5NO_2$. Freed's theory [12] of the pressure saturation of lifetimes was developed for small and intermediate

TABLE 2

Molecular constants of the quenchers and the collisions required to quench the $^1A_2$ and $^3A_2$ states of CS_2 at 4480 Å

Collision partner	Dipole moment μ [a] (debye)	Polariz- ability α (Å³)	Lennard-Jones diameter d_{LJ} (Å)	Ionization potential I_P [a] (eV)	Collisions to quench at 4480 Å [b]	
					$^3A_2$	$^1A_2$
O_2	0	1.61[c]	3.433[d]	12.06	3.2	0.9
$C_2H_5NO_2$	3.65	10[e]	6.2[e]	10.88	0.8	0.2
CS_2	0	8.78[c]	4.44[d]	10.08	—	—
CO_2	0	2.66[c]	3.996[d]	13.77	2.7	0.8
NO	0.153	1.76[c]	3.47[d]	9.25	3.0	0.9
CH_3OH	1.70	3.32[e]	3.585[d]	12.3	0.7	0.2
CCl_4	0	10.53[c]	5.881[d]	11.48	3.0	0.8
C_2H_5OH	1.69	5.11[e]	4.455[d]	11.0	1.1	0.2

[a]From ref. 15.
[b]The collision frequency at 300 K is $7.85 \times 10^{-11} d_{AB}^2 / \mu_{AB}^{1/2}$ collisions cm^3 molecule^{-1} s^{-1} where d_{AB} is the mean molecular diameter in ångströms and μ_{AB} is the collision-reduced mass in atomic mass units.
[c]Calculated from the values of the refractive index given in ref. 15.
[d]From ref. 16.
[e]From ref. 14.

molecules, and it deals with the high pressure saturation of collisionally induced intersystem crossing. A possibility is that this effect occurs for quenching by $C_2H_5NO_2$ because of the high dipole moment of this quencher. In the case of quenching by O_2 it is possible that a chemical reaction channel between O_2 and excited CS_2 [17] is available, and the quenching would then follow the route

$$CS_2 + h\nu \rightarrow CS_2{}^*$$

$$CS_2{}^* + O_2 \begin{cases} \rightarrow CS_2 + O_2 \\ \rightarrow CS + SO_2 \\ \rightarrow polymer \end{cases} \qquad (6)$$

Similar behaviour has been observed by Wampler *et al.* [18] for the quenching of UF_6 by various quenchers.

The saturation effect should occur for all the quenchers at sufficiently high pressures, but under these conditions the emission from CS_2 is too weak to be detected. This effect is observed when the emission is detected at the shorter wavelength for $C_2H_5NO_2$ because the density of final states for the transition is higher. For the same reason, the quenching cross sections are larger for the emission at 4480 Å. This effect may also occur for emissions at longer wavelengths, but it requires pressure conditions for which the emission is too weak to be detected.

For O_2, the saturation effect is observed at both 4480 and 5860 Å because it is produced by a different mechanism from that for $C_2H_5NO_2$.

Tables 1 and 2 show that, as expected, the quenching cross sections for the fast component are much higher than those for the slow component. The experimental cross sections for the short-lived state ($^1A_2$) are a factor of 4 or 5 greater than the gas kinetic values for quenchers with high dipole moments, which shows the importance of that parameter in the quenching of singlet states. The number of collisions required to quench the $^3A_2$ state is a factor of 4 greater than that required to quench the $^1A_2$ state.

We now focus our attention on applying the model of Thayer and Yardley to our system. As can be seen in Fig. 6, the cross sections for the polar collision partners are not well correlated; however, if eqn. (4) is used (Fig. 7) the cross sections for all the quenchers are correlated which shows that the model gives a good description of our system, as it does for propynal [11] and glyoxal [14]. These results show that the factor $(D_P{}^{kf})^2(S^{1k})^2(E_i{}^0 - E_k{}^0)^{-1}$ is very small for CS_2, propynal and glyoxal where the collisional deactivation of the singlet state results primarily in the formation of molecules in the triplet state.

As we know, A is a constant that depends on the effective density of states of the final state of the transition. We estimated A for the fast and slow components and found the ratio A_f/A_s to be of the order of 4, which is consistent with the higher value of the final density of states for the transition corresponding to the fast component compared with that for the transition corresponding to the slow component.

The estimated value for A_s at 4480 Å is higher than that for 5860 Å which shows that the latter corresponds to a transition from lower vibrational levels of $^3A_2$. A similar result is obtained for A_f, and therefore vibrational relaxation should occur in both electronic states as has been pointed out previously [9].

Acknowledgment

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