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SO₂ REVISITED: LASER SPECTROSCOPY OF COLD MOLECULES AND COLLISION-INDUCED ELECTRONIC AND ROTATIONAL RELAXATION*

EDWARD K.C. LEE, BRUCE G. MACDONALD and DENNIS L. HOLTERMANN
Department of Chemistry, University of California, Irvine, CA 92717 (U.S.A.)
ROGER NANES
Department of Physics, California State University, Fullerton, CA 92634 (U.S.A.)

Summary

SO_2 has an electronic absorption band in the UV and some of the rotational structures between 3000 and 3300 Å have been assigned to the $\tilde{A}\ ^1A_2 \leftarrow \tilde{X}\ ^1A_1$ transition by Hamada and Merer (in 1974 - 1975). It is believed that the $\tilde{B}\ ^1B_1 \leftarrow \tilde{X}\ ^1A_1$ transition also lies in this wavelength range but extensive perturbations of the $\tilde{B}$ state by the $\tilde{X}$ state have prevented its rotational analysis. In an attempt to locate vibronic origins of the two overlapping transitions, we took rotationally resolved fluorescence excitation spectra of cold SO_2 molecules (at about 1.0 K) in a supersonic free jet. The rotational structure is greatly simplified and typical vibronic bands consist of from three to five rotational lines, the $^rR_0(0)$ line being the most intense. Numerous new vibronic features are readily recognized and they make a more precise vibrational assignment possible. In the selective excitation of single rotational levels of the $\tilde{A}\ ^1A_2$ state, the lifetime as well as the intensity distribution of rotationally resolved fluorescence emission were measured as a function of pressure. Collisional electronic quenching by polar molecules is very efficient, reaching a maximum value about 10 times greater than gas kinetic values. Collisional rotational relaxation proceeds by a dipole-type mechanism with a state-to-state cross section of about 50 Å² for $\Delta K_a = +1$ or $\Delta K_a = -1$.

1. Introduction

The importance of SO_2 in the theory of radiative and radiationless transitions [1 - 5] has prompted this investigation of laser-excited fluorescence emission from selected rotational levels of SO_2 excited in the 3000 - 3300 Å region. Some of the rotational structures of the electronic absorption band in this wavelength region have been assigned to the $\tilde{A}\ ^1A_2 \leftarrow \tilde{X}\ ^1A_1$ transition by Hamada and Merer [6, 7]. It is believed that the $\tilde{B}\ ^1B_1 \leftarrow \tilde{X}\ ^1A_1$ transition also lies in this wavelength range but massive perturbations of $\tilde{B}\ ^1B_1$ by $\tilde{X}\ ^1A_1$ through

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Renner–Teller interaction have prevented its rotational analysis. In an attempt to locate vibronic origins of the two overlapping transitions, we obtained rotationally resolved fluorescence excitation spectra of cold SO_2 molecules (about 1.0 K) in a supersonic free jet. The rotational structure in the fluorescence excitation spectrum is greatly simplified and typical vibronic bands consist of from three to five rotational lines, with the $^rR_0(0)$ line being the most intense. Numerous new vibronic features are readily recognized, and they make a more precise vibrational assignment possible. Furthermore, the lifetimes and the intensity distributions of the rotationally resolved fluorescence emission from selected rotational levels of $\tilde{A}\ ^1A_2$ were measured as a function of pressure at room temperature, in order to study the variation of the collision-induced energy transfer processes (including electronic and rotational relaxation) by a variety of collision partners. We have extended our measurements considerably since the report of our preliminary studies [8, 9]. The collision-free lifetimes of single rotational levels (SRLs) vary from 15 μs for E band excitation [8] at 3043 Å to 49 μs for (1, 4, 1) band excitation at 3273 Å. We attribute the shorter lifetime at higher excitation energy to the greater mixing of zero-order B_1 character into the zero-order A_2 state. It was found also that electronic quenching by highly polar collision partners (with no possibility for resonant intermolecular energy transfer) occurs with a cross section about 10 times greater than the gas kinetic collision cross section (50 Å^2) whereas state-to-state rotational relaxation for $\Delta K_a = \pm 1$ occurs with a cross section nearly equal to the gas kinetic collision cross section. Noble gas and nonpolar collision partners are an order of magnitude less efficient in energy transfer. We attribute the observation of propensity for the collision-induced $\Delta K_a' = \pm 1$ rotational transitions in SO_2^* to a long-range dipole–dipole type of mechanism. Collision-induced rotational transitions of polar molecules in the ground electronic state have been known to involve a dipole-type mechanism from microwave double-resonance experiments (for a review see ref. 10) and collisional line-broadening studies in microwave spectroscopy (for reviews see ref. 11). The observed parallel between the collision-induced electronic-quenching cross section and the collision-induced $\Delta K_a' = \pm 1$ rotational transition may be regarded as a collision-broadened radiationless transition mechanism for intermediate case molecules.

2. Experimental details

Resolved fluorescence from an SRL of SO_2 ($\tilde{A}\ ^1A_2$) was monitored after narrow-band laser excitation between 3000 and 3300 Å. A frequency-doubled flashlamp-pumped dye laser (Chromatix CMX-4) with an intracavity etalon produced UV output pulses of 0.03 - 0.3 mJ, approximately 1 μs duration and 0.2 cm^{-1} or less full width at half-maximum (FWHM). A large volume multipath absorption and/or fluorescence cell with spherical mirrors separated by 29 cm was used for a long path length of absorption while maintaining a high collection efficiency of the fluorescence to be imaged into a 1 m monochromator. The emission was analyzed in second order with a dispersion of 4 Å mm^{-1} and detected by a photomultiplier (PMT) with an S-20 response (EMI 9558QB).

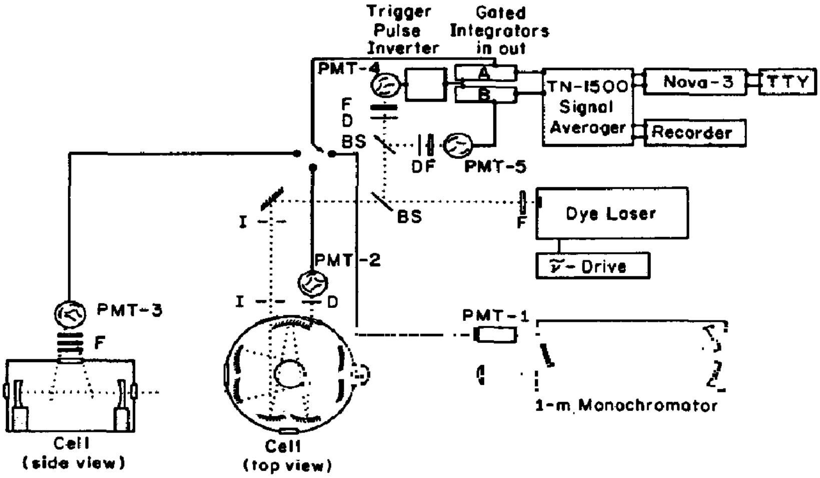

Fig. 1.

The experimental set-up for rotational relaxation studies is shown in Fig. 1. The laser and the fluorescence output signals from the PMTs were fed directly into a pair of gated current integrators and were averaged over a preset number of laser pulses using a digital signal averager (Tracor Northern TN-1500). The ratio of the fluorescence to the laser intensity was recorded, while the monochromator scanned the emission wavelength. The experimental set-up for fluorescence lifetime studies was identical except that a 100 MHz waveform recorder (Biomation 8100) was used to monitor the time dependence of the signal in place of the gated integrator. The fluorescence decay was recorded while the monochromator was set at a frequency corresponding to a given rovibronic transition. Studies were made in an SO_2 pressure range from 0.1 to 7 mTorr.

Excited state rotational levels of interest were identified from fluorescence excitation spectra. In most cases, excited state levels were reached by excitation in the ^{P}P subbranches where the line density in absorption is relatively low compared with that at the band center and for which some rotational assignments have been made [6, 7]. In some instances "unassigned" transitions were excited for comparison against the assigned features.

The rotationally cold supersonic beam of SO_2 was obtained by a free jet expansion (for a review see ref. 12) of the He–SO_2 mixture (2 - 30 atm) through a 50 μm nozzle. An Nd–YAG laser-pumped dye laser (Quanta Ray DCR-1A and PDL-1) with a pressure-tuned intracavity etalon and a second-harmonic generation crystal produced UV output pulses of approximately 1 mJ, about 7 ns duration and 0.2 cm^{-1} or less FWHM. The fluorescence excitation spectra between 3000 and 3250 Å and the time-resolved fluorescence were measured using the Quanta Ray laser, a boxcar averager (Princeton Applied Research models 162 and 164), and the waveform recorder and signal averager combination described above.

3. Results and discussion

The 2900 Å system of SO_2 has been extensively studied as an illustrative example of the "Douglas effect" [1], *i.e.* the anomalous lifetime behavior of the fluorescence [2]. Brus and McDonald [13] and Calvert and his coworkers [14] have shown in their fluorescence decay studies at various excitation wavelengths that non-exponential decay of the total emission intensity is made up of two decay components. The short-lived component with the lifetime τ_S was attributed to the $^1A_2$ state while the long-lived component with the lifetime τ_L was attributed to the overlapping $^1B_1$ state perturbed by Renner–Teller coupling with the dense manifold of the isoenergetic levels of the $^1A_1$ ground electronic state. These studies presented what was thought to be crucial evidence of the two emitting states. However, the studies were carried out with relatively broad-band laser excitation (3 - 10 cm^{-1}) which is clearly inadequate for selective excitation to an SRL [4] and also with insufficient spectral resolution to distinguish the fluorescence from the two emitting states $^1A_2$ and $^1B_1$. In our preliminary study of the Clements E band [8] we established the importance of utilizing selective excitation of an SRL together with rotationally resolved fluorescence emission spectroscopy to differentiate between these two emitting electronic species. We have applied the same technique extensively to study a number of other vibronic levels as discussed below.

3.1. Emission spectra

Vibrationally resolved fluorescence emission from SRL excitation of the vibronic band of interest in the 3000 - 3300 Å region was first recorded at low spectral resolution, and these survey spectra were found to be similar to the fluorescence emission spectra obtained from single vibronic level (SVL) excitation by Shaw *et al.* [15, 16]. The two most intense vibronic emission bands terminate to the (1, 0, 0) and (2, 0, 0) vibrational levels in the ground electronic state as shown in Fig. 2 for the E band excitation. Under higher spectral resolution, the

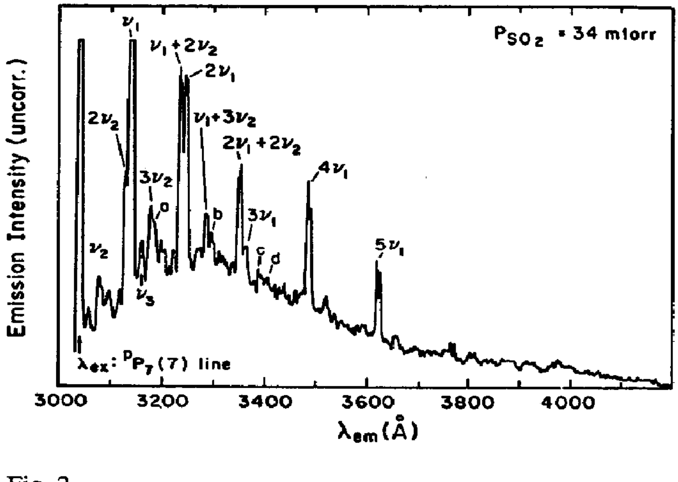

Fig. 2.

TABLE 1

Excitation wavelength λ_{ex} dependence of our SRL values of the $SO_2(^1A_2)$ self-quenching rate constant k_Q and extrapolated zero-pressure lifetime τ^0 compared with the values of τ_S and τ_L reported by others

λ_{ex}(Å)	*This work*[a]		*Reference 13*		*Reference 14*	
	k_Q (μs^{-1} Torr^{-1})	τ^0 (μs)	τ_S (μs)	τ_L (μs)	τ_S (μs)	τ_L[b] (μs)
3273	55	49			18 ± 16	180 ± 50
3252	45	30			27 ± 16	110 ± 30
3226	64	34	25	240	19 ± 8	140 ± 30
3210	61	32			17 ± 8	250 ± 40
3107(B)	83	17			40 ± 10	320 ± 20
3043(E)	67	15	48.8	308	83 ± 11	180 ± 10
3001(G)	82	21	42.1	309	43 ± 28	240 ± 20

[a] The values listed are in some cases the average value for several SRLs.

[b] The intensity parameter $I_L/(I_L+I_S)$ varies from 0.44 (3225 Å) to 0.92 (3020 Å) for mechanism II and from 0.26 (3225 Å) to 0.51 (3020 Å) for mechanism III (see ref. 14).

(1, 0, 0) band is separated into its r-form and p-form subbranch rotational components of approximately equal intensity, as shown in Fig. 3.

3.2. *Fluorescence lifetimes*

The time-resolved fluorescence intensity measurements were carried out by monitoring the rotationally resolved p-form subband emission terminating to the (1, 0, 0) level with a 3 Å (or 6 Å) bandpass of the monochromator. The fluorescence decay from every rotational level excited was found to be *single exponential* over four lifetimes. A brief summary of the extrapolated zero-pressure lifetimes τ^0 and the self-quenching rate constants k_Q for various excitation regions is given in Table 1, together with a few τ_S and τ_L values reported by Brus and McDonald [13] and Su *et al.* [14] for comparison. Our rate constants listed in Table 1 are dominated by electronic quenching of the $^1A_2$ state but other "non-specific" energy transfer processes make a small contribution to the rate constant. These "non-specific" processes include vibrational relaxation and any rotational relaxation which occurs with a broad distribution of final rotational states in contrast with that which occurs with a narrow distribution by the $\Delta K_a = \pm 1$ propensity rule for a dipole-type mechanism.

If we compare our SRL values of τ^0 with the values of τ_S reported by Brus and McDonald [13] and Su *et al.* [14], it is clear that the trends of the excitation wavelength dependence are quite opposite. The implication is that we are sampling a very different excited state than Brus and McDonald and Su *et al.* have sampled as a result of the different laser bandwidths used. If we take our value of τ^0 to be representative of the selected "relatively pure" $^1A_2$ state, it appears that they have measured the fluorescence decay of an ensemble of rotational levels with a wide distribution of lifetimes or a wide range of A_2 and B_1 character. Any further analysis of this complicated situation is probably futile. Since most of our samples were selected from the group of relatively unperturbed rotational levels assigned to the $^1A_2$ state by Hamada and Merer [6] and also we have locked into the sharp emission feature with single-exponential decay rather than the broad underlying continuum, we are working with what is believed to be a set of "relatively pure" $^1A_2$ levels, free from contamination by, presumably prevalent, nearby $^1B_1$ levels.

We attribute the lifetime of about 50 μs that we obtained in the longest excitation wavelength region (3273 Å) to the unperturbed $^1A_2$ state of (1, 4, 1) vibration. This level is certainly below the suggested electronic origin of the $^1B_1$ state (3220 Å by Brus and McDonald [13], 3100 - 3160 Å by Hamada and Merer [7] and 3200 Å by Shaw *et al.* [16]). At shorter wavelengths (above the $^1B_1$ origin), there is a distinct possibility of greater mixing of $^1B_1$ with $^1A_2$.

Hamada and Merer [7] recognized the possibility of observing the $K' = 0 \leftarrow K'' = 1$ subband of the $^1B_1 \leftarrow {}^1A_1$ transition, since $K' = 0$ in this transition ($\tilde{B} \leftarrow \tilde{X}$) should be immune from the Renner–Teller coupling. They were unable to obtain evidence for this transition. It is expected that the unperturbed $^1B_1$ ($K' = 0$) levels should have a normal radiative lifetime whereas the perturbed $^1B_1$ ($K' \geqq 1$) levels should have an anomalously long radiative lifetime [1]. The exact nature of the mixing of $^1A_2$ with $^1B_1$ is not known, but an interesting situation arises if $^1A_2$ is mixed with the unperturbed $^1B_1$ ($K' = 0$) levels as well as the perturbed $^1B_1$ ($K' \geqq 1$) levels. Strickler and Howell obtained a calculated radiative lifetime of 0.6 μs using the integrated absorption coefficients for the entire 2900 Å system [17], and one might expect this magnitude of lifetime to be applicable to the unperturbed $^1B_1$ levels. It is probable that the lifetime of the severely perturbed B_1 levels is represented by the value of τ_L in the 200 - 300 μs range shown in Table 1. It is possible to speculate on the lifetime variation among the $^1A_2$ levels that we have sampled from the foregoing discussion. We should expect a correlation of shorter lifetimes with the $^1A_2$ levels having greater *unperturbed* $^1B_1$ character and smaller *perturbed* $^1B_1$ character. A trend is observed for shorter lifetimes at higher excitation energy (see Table 1), suggesting greater mixing with unperturbed $^1B_1$ (and lesser mixing with perturbed $^1B_1$) at higher excitation energy in our sampled levels. Our sampling preference for excitation of a rotationally analyzed level [6, 7] and an observation of the discrete rotationally resolved emission bands probably biases our data against the possibility of sampling the $^1A_2$ levels greatly mixed with perturbed $^1B_1$ levels. It is probable that Brus and McDonald [13] and Su *et al.* [14] have sampled favorably the latter levels.

3.3. *Collision-induced rotational relaxation*

We reported with the preliminary results of the investigation [9] on collision-induced rotational transitions from a selected J', K' level in the E band near 3043 Å that a propensity for $\Delta K_a' = \pm 1$ exists in the collision with ground state SO_2 molecules. The state-to-state cross sections $\sigma_{0,+1}$ and $\sigma_{0,-1}$ for collisional up-pumping and down-pumping respectively were determined to be about 50 Å^2. This investigation was extended to an SRL in the B band (3107 Å) whose p-form emission feature terminating to the (1, 0, 0) level gives a greater frequency separation between the intense resonance emission line and the collisionally induced

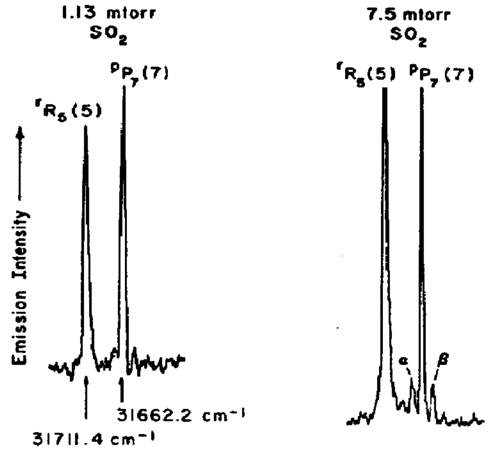

Fig. 3.

emission lines α and β for $\Delta K_a' = -1$ and $\Delta K_a' = +1$ transitions respectively than the previous studies near 3043 Å shown in Fig. 3. This allowed a more precise determination of the relative populations of collisionally pumped rotational levels as a function of pressure and hence a more precise determination of "specific" rotational relaxation cross sections for $\Delta K_a' = \pm 1$. The results obtained with the B band excitation are presented for three collision partners, argon, SO_2 and CH_3NO_2, in Table 2 together with the result for SO_2 obtained previously with the E band excitation [9].

We have not observed clear evidence of collision-induced $\Delta K_a' = \pm 2$ transitions or broadening of the p-form resonance emission features due to collision-induced $\Delta J'$ transitions. These observations are consistent with the dipole-type collision-induced rotational transitions expected [10] for a molecule like SO_2 with a dipole moment along the b axis and zero nuclear spin for oxygen atoms. The observed state-to-state rotational relaxation cross sections for SO_2 and CH_3NO_2 in the B band excitation via ${}^pP_{10}(10)$ are about half as large as that for SO_2 in the E band excitation via ${}^pP_7(7)$. The $\Delta K_a' = \pm 1$ gaps about $K_a' = 9$ reached by ${}^pP_{10}(10)$ are greater than the $\Delta K_a' = \pm 1$ gaps about $K_a' = 6$ reached by ${}^pP_7(7)$, and therefore a smaller energy transfer efficiency is expected

TABLE 2

Collision-induced state-to-state rotational relaxation cross sections at 23 °C

λ_{ex}(Å)	*Excitation transition*	*Collision partner*	$\sigma_{0,-1}$ (Å^2)
3107 (B)	${}^pP_{10}(10)$	SO_2	28
		CH_3NO_2	27
		Ar	4
3043 (E)	${}^pP_7(7)$	SO_2	50

for the former if the energy gap law is applied. The observation is therefore consistent with the expectation.

3.4. *Collision-induced electronic quenching*

The collisional quenching of fluorescence from excited molecules has been studied both theoretically [2, 18, 19] and experimentally [20 - 26] with small and intermediate case molecules in connection with the theory of radiationless transitions. Several models have been proposed for correlating the electronic quenching cross sections for polar and non-polar collision partners with molecular properties such as molecular size, polarizability, dipole moment and ionization potential. However, lack of experimental data for a broad range of excited molecules and quenching collision partners has hindered rigorous testing of these models.

Although the quenching of fluorescence from singlet excited SO_2 has been studied previously with a few collision partners, the "emitting state" (or states) was not well characterized [14, 27, 28]. We have examined the quenching of SO_2 by a large number of collision partners following an SRL excitation via the ${}^PP_7(7)$ transition in the E band and the ${}^PP_{10}(10)$ transition in the B band. The quenching rate constant k_Q was obtained from the slope of the linear Stern–Volmer plot of the reciprocal lifetime as a function of foreign gas pressure. The quenching cross sections σ_Q are tabulated in Table 3, together with the ${}^3B_1$ state values [29] and the singlet state values for which the "emitting state" is not well defined [14].

TABLE 3

Electronic quenching cross sections σ_Q (Å^2)

M	*This work, λ_{ex} = 3107 Å, ${}^1A_2$ B band*	*Reference 14, λ_{ex} = 3130 Å*		*Reference 29, λ_{ex} = 3838.8 Å, ${}^3B_1$*
		S component	*L component*	
He	32			
Ne	66			
Ar	99	690	8.9	0.017
Xe	126			
H_2	50			
N_2	124	570	10.4	0.031
O_2	107	490	10.4	0.032
CO	134	860	13.4	0.031
NO	117			22.7
CO_2	198	2000	30.7	0.039
OCS	282			
CH_4	99			
CF_4	139			
SO_2	584	2840	38.9	
CH_2F_2	583			
CH_3CN	804			
CH_3NO_2	863			
C_3H_8	181			

The phosphorescence quenching data for the $^3B_1$ state reported by Sidebottom *et al.* [29] show that the triplet quenching cross sections are three to four orders of magnitude smaller than our values of the $^1A_2$ quenching cross sections, as shown in Table 3, except for NO. The triplet quenching efficiency of NO is three orders of magnitude higher than that of the other collision partners but it is only one-fifth as high as the $^1A_2$ quenching efficiency. Clearly, NO as a free radical quenches the $^3B_1$ state very effectively with a collision efficiency of about 1/2. No such enhanced quenching efficiency for the $^1A_2$ state is observed. The quenching data of Su *et al.* [14] are listed for both the short-lived component and the long-lived component, but neither set agrees with our quenching data for the $^1A_2$ state. Their quenching cross sections for the long-lived component are about a factor of 10 too low compared with our values and those for the short-lived component are about a factor of 5 too high. We feel that the former represents the quenching cross sections of the $^1B_1$ state and reflects the efficiency of the "irreversible" collisional relaxation (vibration and rotation) of the hot ground state which is coupled to the $^1B_1$ state by the Renner–Teller interaction. However, it is difficult to say much about the latter since the short-lived component is the minor constituent of the emitting states and the deconvoluted kinetic data do not have much quantitative significance.

Our values of the $^1A_2$ quenching cross sections show an increasing trend with the polarizability and the dipole moment of the collision partner M. Those with a large dipole moment value (OCS, 0.712 debye; SO_2, 1.63 debye; CH_2F_2, 1.97 debye; CH_3CN, 3.92 debye; CH_3NO_2, 3.46 debye) have cross sections exceeding the values of the kinetic hard sphere cross sections by a factor of 5 - 10. This behavior can be satisfactorily explained by a model involving long-range interactions in which the dipole–dipole contribution plays the dominant role for highly polar molecules. The dipole–polarizability and the dipole–quadrupole interactions are important in collisions with non-polar molecules. Since resonant electronic energy transfer from $SO_2(^1A_2)$ to the various collision partners is not energetically possible, we suggest that the collisional excitation transfer proceeds via an intramolecular process rather than intermolecular process. Thayer and Yardley [22] found that the singlet excited propynal molecules were efficiently quenched by collision partners with large dipole moments. They explained that the quenching occurs by an intramolecular energy-conserving transition induced via the dipole moment of the quenching molecule. Freed explained the collision-induced S–T intersystem crossing in glyoxal by a model involving collisional broadening of the nearly degenerate rotational levels [19]. The trend we observe for electronic quenching cross sections parallels the trend obtained in the variation of cross sections associated with microwave line broadening caused by a long-range dipole interaction mechanism. Therefore, we propose that the electronic quenching of the $^1A_2$ state involves collisional broadening which enhances mixing of $^1A_2$ and $^1B_1$ (and/or $^1A_1$) levels.

Acknowledgments

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