

Relaxation in the 1A_u state of glyoxal. II. Collisional quenching

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Cross sections are reported for collisional quenching of low-lying levels of the 1A_u state of glyoxal by 24 collision partners at 297 °K. The quenching cross sections varied from 1 to 22 Å² with polar collision partners exhibiting the larger cross sections. The quenching rate constants were determined by measuring the time-resolved decay of laser-excited glyoxal, as a function of quench gas pressure. Studies of 3A_u state production for five of these gases indicate that the principal collisional loss channel from the 1A_u state is to the 3A_u state. The derived quenching cross sections are well parameterized by several differing quenching models, not all of which should be valid in this case; such correlations have predictive value, but cannot be taken to verify the quenching model.

I. INTRODUCTION

The collisional quenching of luminescence from small molecules and atoms has been studied^{1,2} for many years. Rössler³ and Selwyn and Steinfeld⁴ have proposed correlations between cross sections for quenching by nonpolar molecules and such basic molecular parameters as dipole polarizability, molecular size, and ionization energy. While these models provide a good correlation for most available data, the lack of data for a broad range of quenching molecules has prevented rigorous testing of the predictions. The quenching of propynal by 19 collision partners with cross sections of 8–175 Å² has been reported by Thayer and Yardley,⁵ who also proposed a new model^{5,6} for correlating the quenching behavior of both polar and nonpolar molecules.

Quenching of the 1A_u state of glyoxal has been shown by Anderson *et al.*^{7,8} to result in the population of the 3A_u state. The 3A_u – 1A_g band system of glyoxal has been studied in absorption,⁹ emission,¹⁰ and magnetic rotation,¹¹ and is well characterized spectroscopically. Yardley¹² has shown that the collision-free lifetime of the 3A_u state is 3.29 msec and also has reported collisional quenching rate constants for this state. The quenching of 1A_u glyoxal has also been studied by Yardley *et al.*¹³ for seven collision partners.

Anderson *et al.*^{7,8} utilized continuous excitation of the 1A_u – 1A_g transition to populate the excited state and assigned the emission from 5175 to 5225 Å as 3A_u – 1A_g emission, dominated by the 0–0, 7_1^1 , 12_1^1 , and other bands. All emission blue of this region was assigned to 1A_u – 1A_g fluorescence, since vibrational relaxation within the 3A_u should be fast under typical experimental conditions. One may also separate 1A_u and 3A_u emission by taking advantage of the three orders of magnitude difference in their lifetimes. Such separation has been done by Dong and Ramsay¹⁴ who modulated the excitation source at 100 kHz and used phase-sensitive detection of the emission to effect the separation.

In this paper we report the quenching of low-lying levels of the 1A_u state by 24 different gases. A nitrogen laser-pumped dye laser populates the 1A_u state in 10 nsec, and the resulting emission is separated into fluorescence (1A_u – 1A_g) and phosphorescence (3A_u – 1A_g) on the

basis of lifetime. For example, Fig. 1 depicts the emission in the vicinity of the 3A_u – 1A_g band system origin in time intervals 0–5 and 25–1000 μsec following laser excitation¹⁵ of the 1A_u state vibrationless level at a pressure of 100 mTorr, where vibrational energy transfer¹⁶ is rapid. The early time component intensity distribution is quite different from that of the late time component, and consists of emission from unidentified vibrational levels of the 1A_u state. All long-lived emission in this region corresponds to well-known bands of the 3A_u – 1A_g system and may therefore be used to monitor the population of the 3A_u state under conditions of rapid vibrational equilibration. The data presented here result in rate constants for loss of 1A_u glyoxal for the various collision partners. In addition, we report measurements of relative rate constants for collisional production of 3A_u glyoxal for five collision partners.

II. EXPERIMENTAL

The apparatus used for the observations reported here has been previously described in detail.¹⁵ A dye laser is used to excite glyoxal vapor at the peak of the 1A_u – 1A_g 0–0 absorption band near 4550 Å. The vibration relaxation time is short¹⁶ compared to the lifetime of the excited levels at all but the lowest pressures used here; therefore, the observed electronic relaxation originates from a Boltzmann thermal distribution of 1A_u levels even though only the vibrationless level is directly populated. It is assumed that this distribution is the same for all collision partners.

For these data the undispersed emission from glyoxal was detected by a 1P28/V1 photomultiplier tube normal to the laser beam. To study the decay of the 1A_u state, the photomultiplier signal is digitized with a 100 nsec resolution transient recorder, and the resulting data summed and stored by a small digital computer. Neutral density filters were used to attenuate the laser beam at pressures above a few mTorr to avoid saturation of the detection electronics. The first few channels, i. e., up to 0.5 μsec, were typically discarded to allow for recovery of the electronics from the scattered light signal. The various emission bands were also observed through a spectrometer which filters out scattered light when observing more than a few Å from the laser wave-

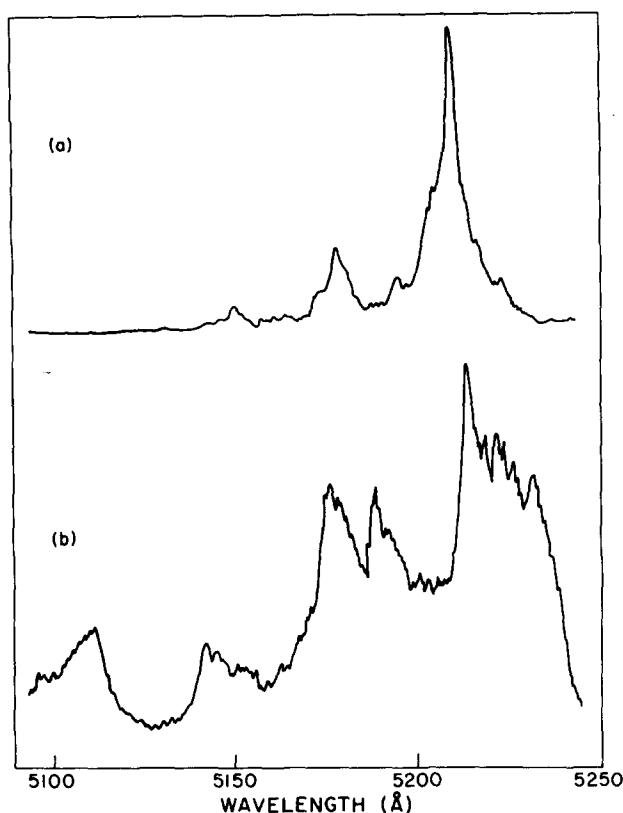


FIG. 1. Emission band structure observed in the time ranges (a) from 25 μsec to 1 msec ($^3A_u \rightarrow ^1A_g$) and (b) up to 5 μsec ($^1A_u \rightarrow ^1A_g$) after pulsed excitation of the 1A_u state of glyoxal at 100 mTorr pressure. The wavelength region shown includes all of the prominent triplet system emission.

length, and it was verified that the early time decay was consistent with that observed by the nonresolved detector after the scattered light effects were negligible.

In order to compare the appearance of phosphorescence with the loss of fluorescence, emission was also viewed through an interference filter centered at 5205 \AA with a 90 \AA bandpass. This filter has a transmission of 35% for both the 0-0 and 7_1^1 $^3A_u \rightarrow ^1A_g$ phosphorescence bands, and less than 0.1% transmission of the principal $^1A_u \rightarrow ^1A_g$ fluorescence bands. A base glyoxal pressure of ~ 120 mTorr was used in these observations to insure complete vibrational relaxation of the 3A_u state molecules before significant emission occurs. The high pressure also reduces excited state diffusion from the field of view of the photomultiplier during 3A_u decay and thus avoids a spurious increase in the phosphorescence signal as the total pressure is increased.

In these studies of phosphorescence, the photomultiplier output signal goes directly to a high gain ($\sim 10^4$) gated integrator constructed around a chopper-stabilized operational amplifier. An electronic switch on the input line is used to integrate the emission in the time interval from 15 to 25 μsec after the laser pulse. On this time scale errors due to quenching of the 3A_u state are negligible.¹² The output of the integrator is sampled by a computer analog-to-digital converter input, summed for a series of laser pulses, and stored.

All quenching molecules which are normally gas phase at room temperature were obtained from lecture bottles. The stated purity of these bottles is in excess of 99% with the exception of N_2O , listed as 98% pure. Those quenching gases which are liquid at room temperature were pumped on and thoroughly outgassed before selecting a sample for quenching. The purity of these samples may be slightly lower than for the gas phase samples, due to the different gas handling technique used. The maximum level of impurity in either case is estimated at less than 3%.

III. COLLISIONAL LOSS FROM THE 1A_u STATE

A. Observations

A glyoxal pressure of about 3 mTorr was used for most of the 1A_u collisional loss rate constant measurements. However, glyoxal pressures as high as 120 mTorr were used with various quenchers to verify that the measured quenching rate constants are independent of glyoxal pressure. Each lifetime was typically measured from the sum of the emission from 500 laser pulses, which resulted in a sufficiently good exponential decay to determine the lifetime to within 1%, with a dynamic range greater than three lifetimes.

Lifetimes were measured for the various collision partners for added pressures between a few and several hundred mTorr. The reciprocal of the lifetime is the total loss rate for radiative and nonradiative processes. Since these loss rates are additive, the value obtained from the pure glyoxal sample may be subtracted to obtain the loss rate due to the added quencher. For all gases studied the loss rate was a linear function of pressure and Stern-Volmer^{1,17} analysis was used to extract the rate constants. Figure 2 depicts typical data for loss of fluorescence with added pressure.

A least-squares fit to these data normally results in a standard deviation of the slope or quenching rate constant of about 1% for 10 added pressure data points. The rate constants are reproducible to better than 5% for most collision partners; repeatability is apparently lim-

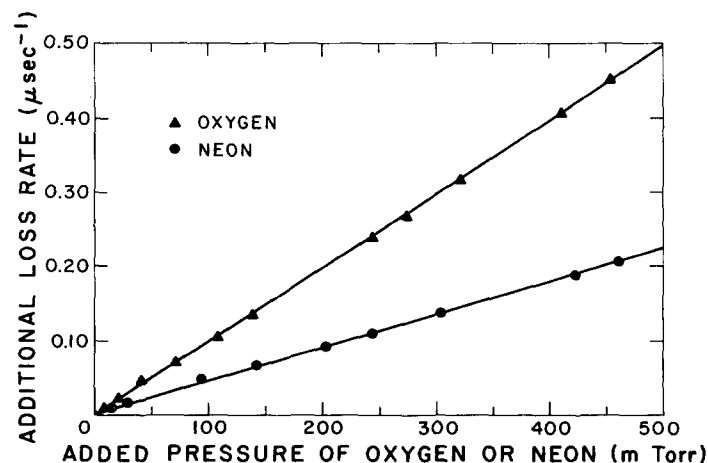


FIG. 2. Stern-Volmer plots for quenching of the low-lying levels of the 1A_u state for two typical gases added to 3 mTorr of glyoxal.

TABLE I. Observed^a quenching rate constants and cross sections for low-lying levels of the ¹A_u state of glyoxal, with molecular constants of quenching gases.

Collision partner	Quenching rate constant ^b 10 ⁻¹¹ cm ³ sec ⁻¹	σ_Q^c (Å ²)	Collisions to quench ^d	Diameter ^e σ_{L-J} (Å)	Polarizability α (Å ³)	Ionization potential ^f (eV)	Dipole moment ^g (Debye)
He	1.7, 1.7 ^h	1.3	26, 26 ^h	2.58	0.204 ⁱ	24.6	...
H ₂	3.5	2.0	20	2.97	0.79 ^j	15.4	...
Ne	1.4	2.1	17	2.789	0.393 ⁱ	21.6	...
D ₂	3.2 ^h	...	16 ^h
Ar	1.8, 2.1 ^h	3.5	12, 10 ^h	3.418	1.66 ⁱ	15.7	...
N ₂	2.2	3.8	12	3.68	1.76 ^j	15.6	...
CH ₄	2.9	4.1	12	3.822	2.62 ^j	12.7	...
Xe	1.8 ^h	...	12 ^h
C ₆ H ₁₂	3.2, 4.3 ^k	7.6	10, 7.4 ^k	6.09	11.00 ^l	10.0	...
CO	2.5	4.4	10	3.59	1.95 ^j	14.1	0.112
C ₂ H ₆	3.0	5.4	10	4.418	4.48 ^j	11.6	...
C ₂ H ₄	3.6	6.3	8.5	4.232	4.26 ^l	11.4	...
CCl ₄	3.6	9.3	8.3	5.881	10.51 ^j	11.47	...
C ₂ Cl ₄	3.8	10.0	7.9	~6.0 ^m	12.1 ^l	9.32	...
O ₂	3.0, 3.3 ^h	5.6	7.8, 7.2 ^h	3.433	1.60 ^j	12.07	...
N ₂ O	3.2	6.5	7.6	3.88	3.00 ^l	12.9	0.167
C ₆ H ₆	5.1	12	5.7	5.27	10.32 ^l	10.32	...
C ₆ H ₅ F	6.4	16	4.6	~5.5 ^m	~11 ^m	9.20	1.60
C ₆ H ₅ Cl	6.6	16	4.6	~5.7 ^m	~12 ^m	9.07	1.69
C ₂ H ₅ NO ₂	9.4	22	3.8	~6.2 ^m	~10 ^m	10.88	3.65
CH ₃ NO ₂	8.8	19	3.7	~5.5 ^m	~5.6 ^m	11.97	3.46
C ₂ H ₂ O ₂	6.3, 6.0 ^h	14	3.7, 3.9 ^h	~4.0 ^m	4.27 ^l	9.48	0
CH ₃ OH	6.8	12	3.7	3.585	3.32 ^j	12.3	1.70
CH ₃ Cl	5.7	12	3.6	3.375	4.55 ^j	11.3	1.87
C ₂ H ₅ OH	7.7	16	3.6	4.455	5.11 ^j	11.0	1.69
CH ₃ CN	9.3	18	3.5	~5.0 ^m	4.53 ^l	12.3	3.92
CH ₃ F	5.9 ^h	...	3.0 ^h

^aThis work except as noted.^bEstimated error ±10%.^cThe quenching cross section at 300 K is $\sigma_Q(\text{Å}^2) = 4.02 \times 10^{10} \mu_{AB}^{1/2} k$, where $\mu_{AB}^{1/2}$ is the collision reduced mass in amu and k is the quenching rate constant.^dThe collision frequency at 300 K is $7.85 \times 10^{-11} \sigma_{AB}^2 / \mu_{AB}^{1/2}$ (collisions · cm³) / (molecule · sec), where σ_{AB} is the mean molecular diameter, $\sigma_{AB} = \frac{1}{2}(\sigma_A + \sigma_B)$ in angstroms, and $\mu_{AB}^{1/2}$ is the collision reduced mass in amu.^eJ. O. Hirschfelder, C. F. Curtis, and R. B. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1954), pp. 1110–1112, 1212–1214, except as noted.^fJ. L. Franklin *et al.*, Natl. Stand. Ref. Data Ser. 26, (1969).^g*Handbook of Chemistry and Physics*, 54th ed., (Chemical Rubber, Cleveland, 1973), p. E114.^hReference 13.ⁱCalculated from *International Critical Tables*.^jExperimental value from J. Applequist, J. R. Carl, and K. Fung, *J. Am. Chem. Soc.* 94, 2952 (1972).^kReference 8.^lJ. O. Hirschfelder, C. F. Curtis, and R. B. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1954), pp. 949–950.^mEstimated from properties of similar molecules.

ited by impurities introduced in the gas handling procedure.

The measured rate constants and quenching cross sections are listed in Table I. Also given are the number of hard-sphere gas kinetic collisions required to quench the ¹A_u state. These latter numbers are calculated from the rate constants using the Lennard-Jones molecular diameters as given in Table I.

The error in the values measured is dominated by the impurities in the quenching gas. Impurities in the lecture bottles are less than 1% for most gases used. Since the rate constants vary by a factor of 4 for the nonpolar molecules, this 1% impurity implies an error as

great as 3%. Reproducibility of the data suggests that impurities from the gas handling give about 5% random variation. Time resolution contributes 1% and pressure measurement up to 3% error. A reasonable estimate for the total error limit for each rate constant is ±10%.

B. Analysis

An early model for the correlation of quenching efficiency was that of Rössler,³ who asserted that the interaction would be proportional to the dipole polarizability α of the quenching molecules and the duration of the collision, i. e., $\mu^{1/2}$, where μ is the reduced mass. A plot of the quenching cross section versus $\alpha\mu^{1/2}$ for the ¹A_u state of glyoxal is shown in Fig. 3. For the nonpo-

lar molecules the correlation is reasonably good; of course, no correlation is expected for quenching by polar molecules.

Recently, two more detailed analyses of quenching efficiency have been proposed.^{4,5} Each assumes that a dispersion force perturbation mixes the initial and final states of the system consisting of the excited molecule and the quenching partner. In both cases it is assumed that only the electronic ground state of the quencher is energetically accessible. A continuum of final states is assumed for the system and the Fermi Golden Rule is applied to calculate the transition rate. In calculating the cross section from the transition rate, a straight-line trajectory with impact parameter greater than the mean molecular diameter is utilized; collisions with impact parameters smaller than this diameter are assumed to quench with an efficiency which is independent of collision partner.

Assuming a simple dispersion force interaction, Selwyn and Steinfeld⁴ find that the cross section should obey

$$\sigma_Q (\text{\AA}^2) \propto A \mu^{1/2} I_Q \alpha_Q / R_c^3, \quad (1)$$

where A is a constant which depends on the molecule and excited state being quenched, μ is the reduced mass, and I_Q and α_Q are the ionization potential and dipole polarizability of the quenching molecule, respectively. R_c is the minimum impact parameter, usually taken as the mean molecular diameter. Steinfeld¹ has shown that the available experimental data for quenching of fluorescence of small molecules fit this analysis quite well. A plot of our 1A_u glyoxal data as a function of this parameterization is shown in Fig. 4. As with the previous model, the nonpolar quenching appears to be described accurately.

A third model has been developed by Thayer and Yardley^{5,6} to correlate their observations for the quenching of propynal by 19 collision partners. Although propynal has a substantial permanent electric dipole moment, 2.46 D, it is assumed that instantaneous dipole-dipole interactions are dominant in the quenching process. In

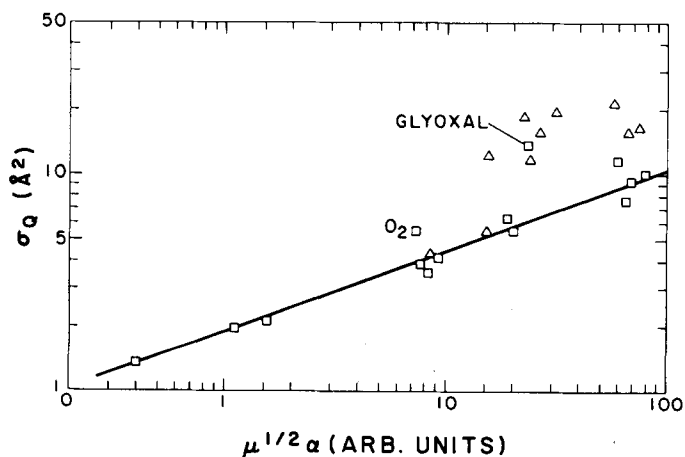


FIG. 3. The cross section for quenching the 1A_u state versus the parameter of Rössler³ for polar (Δ) and nonpolar (\square) molecules.

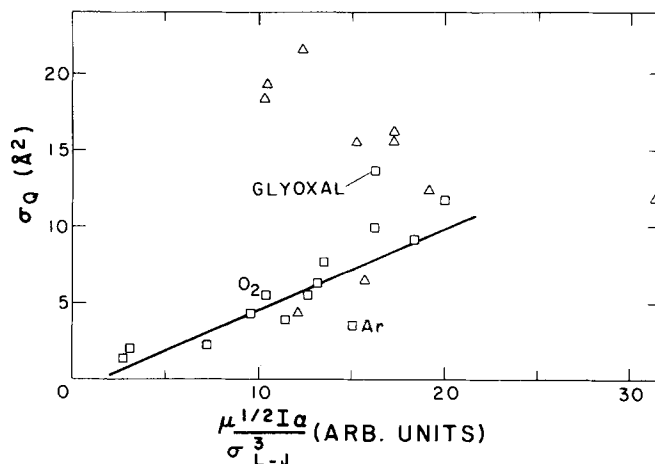


FIG. 4. The cross section for quenching the 1A_u state versus the Selwyn-Steinfeld⁴ parameter for polar (Δ) and nonpolar (\square) molecules.

the initial formulation,⁵ it was also assumed that a spin-allowed transition is involved in the quenching. With these assumptions the cross section is found to be parameterized in the form

$$\sigma_Q (\text{\AA}^2) \propto A \mu^{1/2} \left(\frac{I_E I_Q}{I_E + I_Q} \right)^2 \frac{\alpha_Q^2}{R_c^3} + B \frac{\mu^{1/2} D_Q^2}{R_c^3}, \quad (2)$$

where D_Q is the permanent electric dipole of the quenching molecule; A and B are constants for the particular molecule being quenched, and other notation is as above.

Figure 5 shows a plot of the measured cross section for quenching of the 1A_u state of glyoxal by 24 collision partners, parameterized as indicated by Eq. (2). In addition to good correlation of the nonpolar molecules, the polar quenching partners are also in agreement with predictions in most cases.

Since more recent data⁶ suggest that the quenching in propynal may be a result of intersystem crossing, this parameterization was recently reformulated⁶ to allow for the spin-forbidden process. However, this adds only a factor to Eq. (2) involving among other parts the interaction with an intermediate state. Since correlation

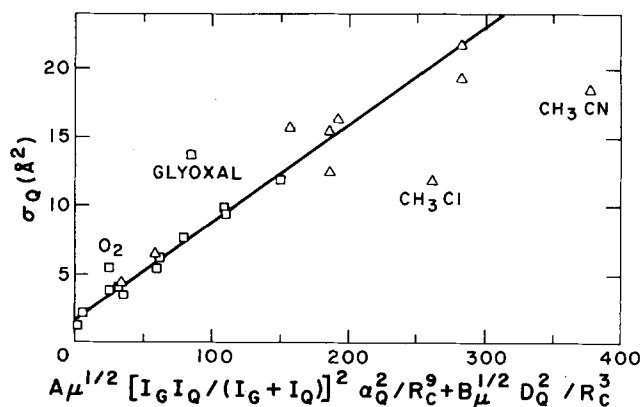


FIG. 5. The cross section for quenching the 1A_u state as a function of the Thayer-Yardley⁵ dispersion force parameter for polar (Δ) and nonpolar (\square) molecules.

with an essentially nonapplicable model is seen above to be quite good, nothing will be demonstrated by utilizing the more correct parameterization.

The molecular constants used for these correlation analyses are given in Table I. Polarizability values unavailable directly were calculated from light refractivity data in the *International Critical Tables*.

C. Discussion

Previous measurements have been made for quenching of the low-lying levels of the 1A_u state by eight different collision partners. These values are also given in Table I. Of the seven rate constants determined from the time-resolved fluorescence studies of Yardley *et al.*,¹³ four were also measured in this work and show good agreement. The other three are also consistent with the quenching trends of this work. The quenching by cyclohexane has also been measured by Anderson *et al.*,⁸ in continuous excitation experiments. The value obtained from that work agrees with the value measured in the present experiment within expected error limits. Frad and Tramer¹⁸ and Beyer *et al.*¹⁵ have reported values for the quenching of single vibronic levels of the 1A_u state; however, as discussed earlier,¹⁵ comparison between those data and the present work is not valid.

Figures 3–5 show that the quenching of 1A_u glyoxal by nonpolar molecules can be parameterized in terms of simple physical constants. Not surprisingly the correlation is better with the second and third models than with the first, since the latter models more explicitly calculate the dispersion force interaction between two molecules. The conclusions that can be made from such good correlations must be examined more carefully.

As will be shown in Sec. IV, the principal path for collisional loss of 1A_u glyoxal is to the 3A_u state, a spin-forbidden process. In a similar study of propynal, Thayer and Yardley⁵ concluded that the observed quenching was not due to intersystem crossing and used the good correlation of the data with the spin-allowed model as a demonstration that this conclusion was correct. Their more recent results⁶ suggest that the propynal quenching is in fact due to intersystem crossing. Thus it appears that the quenching of both glyoxal and propynal are spin-forbidden processes even though both are well correlated by the spin-allowed model.

It is clear that one cannot conclude that a particular model provides an adequate description of the quenching process merely because good correlation with a predicted parameter is obtained. The value of correlating observations in the above manner lies in observing anomalous quenching behavior and relating this observation to molecular parameters or in predicting cross sections for quenching of the state of interest by additional collision partners.

In addition to the polar molecules, which show only fair correlation in some cases, glyoxal self-quenching is prominent as an efficient quencher in all three of the quenching plots. Oxygen also appears to be relatively efficient, especially in Figs. 3 and 5. Possible explanations for this behavior are discussed below.

1. Oxygen quenching

The uniqueness of oxygen as a quenching partner may lie in its triplet ground state, its unpaired electron and associated magnetic effects, or in possible chemical bonding with the excited glyoxal molecules. It will be shown later that the ratio of production of 3A_u state glyoxal molecules to the loss of 1A_u state molecules is approximately the same for collisions with oxygen as for four other gases including helium and argon. Thus there is no expectation that any significant fraction of the oxygen quenching is chemical.

The initial state of the collision system consists of the $^3\Sigma_g^-$ ground state oxygen plus the 1A_u state glyoxal. Since the final glyoxal state is the 3A_u , 2800 cm^{-1} below the levels populated by the laser, the $^1\Delta_g$ state of oxygen 8000 cm^{-1} above the ground state is not energetically accessible. Therefore there is no reason to expect an increase in quenching efficiency due to the triplet ground state of oxygen.

In the quenching of smaller molecules such as I_2 , OH, and SO_2 ,¹ oxygen appears to show no increased efficiency. Similarly, in the quenching of the first excited singlet state of propynal⁵ oxygen is well-behaved. In each of these cases quenching involves a transition to a state of different symmetry but with the same multiplicity.

The 3A_u - 1A_g transition observed in glyoxal is made possible by spin-orbit coupling which mixes the 3A_u and 1A_u excited states. The observations reported here indicate that oxygen may cause a spin-orbit perturbation which increases the mixing of the 3A_u and 1A_u states and consequently the quenching of the 1A_u state. This effect may be related to an observation of magnetic field quenching of the 1A_u state reported by Dong and Kroll.¹⁹ They have found that emission from this state is decreased by about 20% when a field of about 1000 G is applied.

2. Glyoxal self-quenching

The high efficiency for quenching of 1A_u glyoxal by 1A_g ground state glyoxal molecules is clearly indicative of a substantial additional interaction between these molecules. One possibility is that of an electronic resonance effect such as may occur in general between any excited state and ground state molecules with a dipole allowed transition between the states.²⁰ However we shall show¹⁶ that the 1A_u - 1A_g transition is too weak for such interactions to be significant in glyoxal.

It is probable that the additional glyoxal-glyoxal interaction is due to hydrogen-bonding forces. These forces would tend both to enhance the effectiveness and increase the range of collisional interactions. The existence of such forces is suggested by glyoxal molecular structure and the rapid polymerization of glyoxal vapor on surfaces.

3. Quenching by polar molecules

Ten polar collision partners were used for quenching glyoxal. Two of these, CO and N_2O , have small permanent dipole moments and are only slightly more efficient than similar nonpolar molecules. Six of the po-

lar molecules have a quenching probability, (number of hard-sphere collisions to quench)⁻¹, in the range 0.26–0.29 per collision and seem to be at essentially a constant limit for efficiency. Self-quenching efficiency by ground state glyoxal molecules is also at this limit. The final two polar molecules, fluorobenzene and chlorobenzene, have a probability of 0.22 per collision, a value which is intermediate between the nonpolar molecules and seven most efficient collision partners.

The lack of good correlation for CH₃Cl and CH₃CN may be due to the apparent quenching limit. If this limit is determined by the excited rovibronic levels of the excited glyoxal molecules, one predicts good correlation only for molecules whose efficiency is less than the limit. Molecules with very strong interactions with the excited glyoxal would then have a cross section less than predicted and show poor correlation.

The nature of the intermolecular interaction of glyoxal with the more efficient quenchers may be either due to the strong electric field associated with a permanent electric dipole at short range or caused by a hydrogen-bonding attraction. If the collisions are dominated by either of these effects, the halobenzene compounds should be less efficient. In these two molecules the permanent dipole is localized and shielded to some extent during collisions opposite the halogen. These two molecules are also unlikely to have the hydrogen bonding characteristics predicted for most of the more efficient molecules.

The above data suggest that the limiting quenching efficiency is determined by the excited rovibronic levels of the ¹A_u state. The quenching limit near 3.7 collisions for deactivation of the ¹A_u state, resulting in production of ³A_u glyoxal, implies that about one fourth of the populated ¹A_u levels have significant ³A_u character from spin-orbit or other mixing of the states. The collisional perturbation then serves to relax the ³A_u state vibrationally and irreversibly and hence quenches the ¹A_u state. In this case molecules which interacted via strong electric dipole moments would have the same limit as the ex-

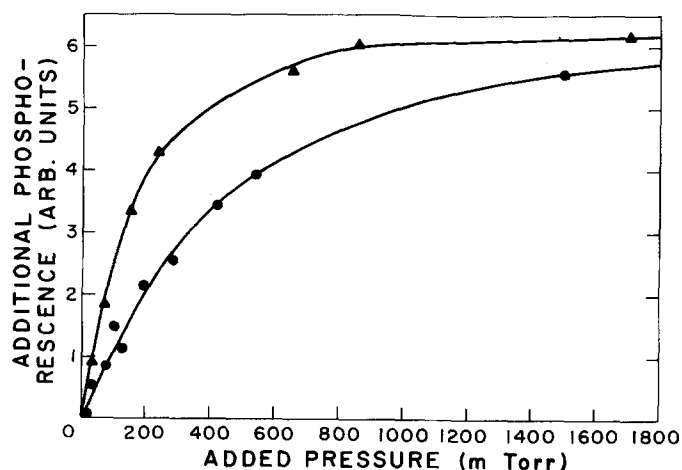


FIG. 6. Additional ³A_u-¹A_g phosphorescence as a function of the added pressure of nitromethane (▲) and argon (●) to 120 mTorr of glyoxal with excitation of the 0-0 ¹A_u-¹A_g band.

TABLE II. Relative rate constants^a after excitation of the vibrationless level of the ¹A_u state of glyoxal.

Collision partner	³ A _u State production	¹ A _u State loss
He	1	1
Ar	1.25 ± 0.25	1.05 ± 0.1
N ₂	1.8 ± 0.5	1.3 ± 0.1
O ₂	1.7 ± 0.2	1.8 ± 0.2
CH ₃ NO ₂	4.9 ± 0.4	5.1 ± 0.4

^aNormalized to helium values.

tremely efficient ¹A_g glyoxal molecules, which apparently interact with hydrogen-bonding forces.

IV. COLLISIONAL PRODUCTION OF THE ³A_u STATE

A. Observations

To obtain the data reported here, the quenching gases were added to a base glyoxal pressure of 120 mTorr and the increase in phosphorescence recorded. Figure 6 shows typical data for phosphorescence increase with added pressure of nitromethane and argon over a limited pressure range. As is seen in the argon data, there is considerable scatter in the region below 300 mTorr. Similar random variations were obtained for most added gases. The results of a least-squares straight line fit made to the low pressure data for five collision partners are given in Table II, normalized to the helium value. Also shown are the relative rate constants for quenching of ¹A_u glyoxal from Table I.

For three collision partners, argon, nitrogen, and nitromethane, a careful check was made to establish that the same limiting value for phosphorescence signal was reached at high pressure. This limiting value is well below any saturation level of the detection system. (Pressures above the 1.5 Torr limit of the capacitance manometer were crudely estimated.) In all cases, the observed signals were normalized to the slightly varying laser power.

Triplet state production was also studied as a function of laser power by inserting neutral density filters in the laser beam. Over about two orders of magnitude in laser power at a pressure of 100 mTorr of glyoxal, the ³A_u production has been found to be linear with laser intensity within the linearity of our integrator.

B. Discussion

As can be seen from Table II, the agreement between the relative production rates of the ³A_u state and loss rates of the ¹A_u state in collisions is quite good. Only for collisions with nitrogen do the measured values not agree well within the expected error limits. The fact that the high pressure phosphorescence quantum yield reaches a constant value which is independent of collision partner shows that quenching of the excited ¹A_u state by atoms, nonpolar molecules, and highly polar molecules is due to the same mixing of states even though there is a difference in behavior and efficiency.

The meaning of the sum of these data is quite clear. The relative loss rate constants from the ¹A_u are the

same as the relative production rate constants for the 3A_u state. This result can be interpreted in two ways. The first is that intersystem crossing is the only non-trivial collisional loss process for excited singlet state glyoxal molecules. The second is that although there are also other channels for loss of 1A_u glyoxal, the branching ratios are independent of collision partner. Since the apparent limit for quenching efficiency of the 1A_u state suggests that relaxation is dependent on the excited 1A_u levels, the second possibility cannot be immediately discarded. For example, if some excited rovibronic levels are intramolecularly coupled to the 3A_u state and others to the 1A_g or other state, the external perturbation (collision) might quench the 1A_u with the same branching ratio regardless of the nature or relative efficiency of the intermolecular perturbation.

In addition to intersystem crossing, the channels most likely for 1A_u glyoxal loss are photochemical decomposition and internal conversion to the 1A_g ground state. There is no evidence for significant photochemistry following excitation of the 1A_u state near the vibrationless level. Also, it has been established²¹ that photochemistry from higher vibrational levels follows intersystem crossing to the 3A_u state. Therefore photochemistry is ruled out as an independent channel.

The density of 1A_g states at the energy of the optically populated 1A_u levels is high enough ($\sim 10^7$ – 10^8 per cm^{-1}) that the statistical limit is expected⁶ to apply. In this case there would be no collisional dependence on the internal conversion rate. Lifetime data¹⁵ for many vibronic levels of the 1A_u state show substantial variations that are suggestive of intramolecular internal conversion. We therefore rule out collisional internal conversion in glyoxal as a significant process and conclude that intersystem crossing to the 3A_u state is the only important channel for collisional quenching of the 1A_u state. This conclusion agrees with the earlier work of Anderson *et al.*⁸

V. PHOSPHORESCENCE FOLLOWING EXCITATION OF THE 1A_u STATE AT LOW PRESSURE

In the study of a similar molecule, biacetyl, it was found²² that there is substantial intramolecular intersystem crossing to the 3A_u state from the 1A_u state. The crossing was attributed²³ to the presence of the 3B_g state, which may lie much higher in energy in glyoxal than in biacetyl. It is also predicted²⁴ that vibrations with b_g symmetry promote intersystem crossing in glyoxal. Thus it is interesting to use the continuous tunability of the dye laser to look for evidence of any intramolecular radiationless transitions over a wide range of excitation.

As shown earlier, collision-induced intersystem crossing is quite efficient. Therefore one must observe behavior at low pressures in searching for intramolecular effects. This means that the signal level to be observed will be quite small and only qualitative observations may be possible. In this series of observations the luminescence was observed broadband as the laser was tuned over the absorption region. The photomultiplier output signal was monitored visually with an oscil-

loscope, since only the existence of long lived emission is of interest. Low level phosphorescence has been observed occasionally in this experiment from small amounts of glyoxal or its polymer on the cell windows. Therefore, care was taken that the windows where the laser was passed into the cell were free of such deposits.

One predicts on the basis of hard-sphere collision rates that at a pressure of 3 mTorr a molecule with a lifetime of 2.4 μsec decays intramolecularly long before any collisions occur. In the case of glyoxal, a phosphorescence signal can be observed exciting either the 0–0 or 8_0^1 absorption bands at this pressure. In both cases the signal vanishes if a sidearm of the cell is cooled with liquid nitrogen. As is seen in the previous paper,¹⁵ the 1A_u state lifetime does appear to be pressure dependent at 3 mTorr.

At pressure slightly below 1 mTorr, exciting and observing as above, no delayed emission was observed above the low background. If the intensity were one fifth that at 3 mTorr it would have been detectable. As the laser was varied continuously from 4550 to about 3700 \AA , no phosphorescence was detected. Higher pressure observations were also made exciting near 3820 \AA , a region of relatively strong absorption. At this wavelength the emission observed was similar to the emission from levels with less energy in the 1A_u state, characterized by some short lived emission and rapid vibrational relaxation to low-lying levels of the 1A_u state. There was no evidence for a significant new channel for decay such as greatly increased intersystem crossing.

Particular care was taken to observe the behavior of emission following excitation of ν_8 , the only b_g symmetry mode, but no differences were found. The wavelengths near 4360 \AA which have been associated with some triplet character, based on magnetic rotational spectra,¹¹ also showed no behavior different from any other levels excited.

VI. CONCLUSIONS

The collisional quenching of low-lying levels of the 1A_u state of glyoxal has been studied for 24 collision partners with quenching cross sections in the range 1.3–22 \AA^2 . It has been shown that the quenching by nonpolar molecules is well correlated with basic molecular parameters for three interaction models. The quenching by polar molecules was also shown to have fair correlation with that model of these three which takes into account the permanent electric dipole moment of the collision partner. However, since the basic assumptions of at least the final model are not valid in the quenching of 1A_u glyoxal, one must conclude that good correlation cannot be used to demonstrate the validity of the correlation model. The correlations are valuable in observing unusual behavior or in predicting cross sections for additional gases.

The most efficient collision partners appear to have reached a limit in probability per hard sphere collision for quenching the 1A_u state. This observation is interpreted as an indication that not all populated rovibronic levels of the 1A_u state are coupled equally well with 3A_u state levels.

Evidence is presented for the existence of substantial long range glyoxal-glyoxal forces, in addition to normal dispersion forces. The correlation diagrams show that glyoxal is more efficient than predicted by a margin unique among the nonpolar molecules and substantially greater than the estimated error limits. It is also noted that collision-dependent $^1A_u \rightarrow ^3A_u$ intersystem crossing is observable at 3 mTorr, at which pressure the mean time between hard collisions is about 10 times the 1A_u state lifetime.

The relative rate of collisional production of the 3A_u state from the 1A_u state has been measured for a range of collision partners. Since other 1A_u loss processes are shown to be unlikely, it is concluded that the principal collisional loss from the 1A_u state is to the 3A_u state. Production of the 3A_u state from the 1A_u state has been observed to require an external perturbation for 1A_u glyoxal with up to 4000 cm^{-1} of excess vibrational energy. Thus glyoxal exhibits small molecular behavior with respect to intersystem crossing over this energy range.

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