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 for many years. Õrstler and Selwyn and Steinfeld 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 propyln by 19 collision partners with cross sections of 8-175 Å² has been reported by Thayer and Yardley, who also proposed a new model for correlating the quenching behavior of both polar and nonpolar molecules.

Quenching of the $^3A_u$ state of glyoxal has been shown by Anderson et al. to result in the population of the $^3A_u$ state. The $^3A_u-^1A_u$ band system of glyoxal has been studied in absorption, emission, and magnetic rotation, and is well characterized spectroscopically. Yardley 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. for seven collision partners.

Anderson et al. utilized continuous excitation of the $^1A_u-^3A_u$ transition to populate the excited state and assigned the emission from 5175 to 5225 Å as $^3A_u-^1A_u$ emission, dominated by the 0-0, 1-1, 2-2, and other bands. All emission blue of this region was assigned to $^1A_u-^3A_u$ 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 Ramsay 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 $^3A_u$ state by 24 different gases. A nitrogen laser-pumped dye laser populates the $^3A_u$ state in 10 nsec, and the resulting emission is separated into fluorescence ($^1A_u-^3A_u$) and phosphorescence ($^3A_u-^1A_u$) on the basis of lifetime. For example, Fig. 1 depicts the emission in the vicinity of the $^3A_u-^1A_u$ band system origin in time intervals 0-5 and 25-1000 μsec following laser excitation of the $^3A_u$ state vibrationless level at a pressure of 100 mTorr, where vibrational energy transfer 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 $^3A_u$ state. All long-lived emission in this region corresponds to well-known bands of the $^3A_u-^1A_u$ 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 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. A dye laser is used to excite glyoxal vapor at the peak of the $^3A_u-^1A_u$ 0-0 absorption band near 4950 Å. The vibration relaxation time is short 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 $^3A_u$ 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 $^3A_u$ 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-
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 N₂O, listed as 98% pure. Those quenching gases which are liquid at room temperature were pumped on and thoroughly outgased 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 the 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 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-

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**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 1. Observed quenching rate constants and cross sections for low-lying levels of the \(^1A_g\) state of glyoxal, with molecular constants of quenching gases.

<table>
<thead>
<tr>
<th>Collision partner</th>
<th>Quenching rate constant (10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1})</th>
<th>(\sigma_{Q}^a \text{ (A}^2)</th>
<th>Collisions to quench(b)</th>
<th>Diameter(c) (\text{A})</th>
<th>Polarizability (\alpha \text{ (A}^3)</th>
<th>Ionization potential(d) (eV)</th>
<th>Dipole moment(e) (Debye)</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>1.7, 1.7(^b)</td>
<td>1.3</td>
<td>26, 26(^b)</td>
<td>2.58</td>
<td>0.204(^4)</td>
<td>24.6</td>
<td>...</td>
</tr>
<tr>
<td>H(_2)</td>
<td>3.2</td>
<td>2.0</td>
<td>20</td>
<td>2.97</td>
<td>0.79(^3)</td>
<td>15.4</td>
<td>...</td>
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<tr>
<td>Ne</td>
<td>3.0</td>
<td>2.1</td>
<td>17</td>
<td>2.789</td>
<td>0.393(^3)</td>
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<tr>
<td>D(_2)</td>
<td>3.2(^b)</td>
<td>...</td>
<td>16(^b)</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
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<tr>
<td>Ar</td>
<td>1.8, 2.1(^b)</td>
<td>3.5</td>
<td>12, 10(^b)</td>
<td>3.418</td>
<td>1.66(^1)</td>
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<td>3.8</td>
<td>12</td>
<td>3.68</td>
<td>1.76(^3)</td>
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<td>CH(_2)</td>
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<td>12</td>
<td>3.822</td>
<td>2.82(^1)</td>
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</tr>
<tr>
<td>Xe</td>
<td>1.8(^b)</td>
<td>...</td>
<td>12(^b)</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
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<td>7.6</td>
<td>10, 7, 4(^b)</td>
<td>6.08</td>
<td>11.00(^1)</td>
<td>10.0</td>
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<td>CO</td>
<td>2.5</td>
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<td>10</td>
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<td>C(_2)H(_2)</td>
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<td>10</td>
<td>4.418</td>
<td>4.48(^1)</td>
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<td>C(_2)H(_4)</td>
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<td>6.3</td>
<td>8.5</td>
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<td>8.3</td>
<td>5.881</td>
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<td>7.9</td>
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<td>12.1(^1)</td>
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<td>O(_2)</td>
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<td>7.7, 7, 2(^b)</td>
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<td>7.6</td>
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<td>C(_2)H(_4)</td>
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<td>12</td>
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<td>5.27</td>
<td>10.32(^1)</td>
<td>10.32</td>
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<tr>
<td>C(_2)H(_6)F</td>
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<td>16</td>
<td>4.6</td>
<td>(-5.5^6)</td>
<td>(-11^6)</td>
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<td>4.6</td>
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<td>(-12^6)</td>
<td>9.07</td>
<td>1.59</td>
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<tr>
<td>C(_2)H(_5)NO(_2)</td>
<td>9.4</td>
<td>22</td>
<td>3.8</td>
<td>(-6.2^6)</td>
<td>(-10^6)</td>
<td>10.88</td>
<td>3.65</td>
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<td>14</td>
<td>3.7, 3.9(^b)</td>
<td>(-4.0^6)</td>
<td>4.27(^1)</td>
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<td>...</td>
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</table>

\(^a\)This work except as noted.
\(^b\)Estimated error \(\pm 10\%\).
\(^c\)The quenching cross section at 300 K is \(\sigma_Q (\text{A}^2) = 4.02 \times 10^{10} \mu_{AB}^{1/2} k\), where \(\mu_{AB}^{1/2}\) is the collision reduced mass in amu and \(k\) is the quenching rate constant.
\(^d\)The collision frequency at 300 K is \(7.85 \times 10^{11} \sigma_{AB}^2 / \mu_{AB}^{1/2} \text{ collisions} \cdot \text{cm}^3 \cdot \text{molecule}^{-1} \cdot \text{sec}^{-1}\), where \(\sigma_{AB}\) is the mean molecular diameter, \(\sigma_{AB} = 1/2 (\sigma_A + \sigma_B)\) in angstroms, and \(\mu_{AB}\) is the collision reduced mass in amu.
\(^h\)Reference 13.
\(^i\)Calculated from International Critical Tables.
\(^k\)Reference 8.
\(^m\)Estimated from properties of similar molecules.

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

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 \(\pm 10\%\).

#### B. Analysis

An early model for the correlation of quenching efficiency was that of R6ssler, who asserted that the interaction would be proportional to the dipole polarizability \(\alpha\) of the quenching molecules and the duration of the collision, i.e., \(\mu^{1/2}\), where \(\mu\) is the reduced mass. A plot of the quenching cross section versus \(\alpha \mu^{1/2}\) for the \(^1A_g\) 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. 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 Steinfeld find that the cross section should obey

$$\sigma_0(\lambda^2) \propto A \mu^{1/2} I_0 \alpha_0 / R_c^2,$$

(1)

where $A$ is a constant which depends on the molecule and excited state being quenched, $\mu$ is the reduced mass, and $I_0$ and $\alpha_0$ 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. Steinfeld has shown that the available experimental data for quenching of fluorescence of small molecules fit this analysis quite well. A plot of our $^1A_g$ 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 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 the initial formulation, 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

$$\sigma_0(\lambda^2) \propto A \mu^{1/2} \left( \frac{I_0 I_Q}{I_0 + I_Q} \right)^2 \frac{\alpha_0^2}{R_c^2} + B \mu^{1/2} \frac{D_0^2}{R_c^3},$$

(2)

where $D_0$ 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 $^1A_g$ 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 data suggest that the quenching in propynal may be a result of intersystem crossing, this parameterization was recently reformulated 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...
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 \( \text{\( ^1 \)} A_g \) 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.,\(^{12}\) 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.,\(^{3}\) 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 Tramer\(^{18}\) and Beyer et al.,\(^{16}\) have reported values for the quenching of single vibronic levels of the \( \text{\( ^1 \)} A_g \) state; however, as discussed earlier,\(^{19}\) comparison between those data and the present work is not valid.

Figures 3–5 show that the quenching of \( \text{\( ^1 \)} A_g \) 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 \( \text{\( ^1 \)} A_g \) glyoxal is to the \( \text{\( ^3 \)} A_g \) state, a spin-forbidden process. In a similar study of propynal, Thayer and Yardley\(^{4}\) 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 results\(^{8}\) 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 unperturbed 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 \( \text{\( ^3 \)} A_g \) state glyoxal molecules to the loss of \( \text{\( ^1 \)} A_g \) 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 \( \text{\( ^3 \)} D_g \) ground state oxygen plus the \( \text{\( ^1 \)} A_g \) state glyoxal. Since the final glyoxal state is the \( \text{\( ^3 \)} A_g \), 2800 cm\(^{-1}\) below the levels populated by the laser, the \( \text{\( ^1 \)} A_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 propynal\(^{6}\) 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 \( \text{\( ^3 \)} A_g \rightarrow \text{\( ^1 \)} A_g \) transition observed in glyoxal is made possible by spin–orbit coupling which mixes the \( \text{\( ^3 \)} A_g \) and \( \text{\( ^1 \)} A_g \) excited states. The observations reported here indicate that oxygen may cause a spin–orbit perturbation which increases the mixing of the \( \text{\( ^3 \)} A_g \) and \( \text{\( ^1 \)} A_g \) states and consequently the quenching of the \( \text{\( ^1 \)} A_g \) state. This effect may be related to an observation of magnetic field quenching of the \( \text{\( ^1 \)} A_g \) 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 \( \text{\( ^1 \)} A_g \) glyoxal by \( \text{\( ^1 \)} A_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.\(^{28}\) However we shall show\(^{16}\) that the \( \text{\( ^3 \)} A_g \rightarrow \text{\( ^1 \)} A_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\(_2\)O, 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)$^3$, 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 CH$_3$Cl and CH$_2$CN 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 $^3A_u$ 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-

<table>
<thead>
<tr>
<th>Collision partner</th>
<th>$^3A_u$ State production</th>
<th>$^1A_u$ State loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Ar</td>
<td>1.25 ± 0.25</td>
<td>1.05 ± 0.1</td>
</tr>
<tr>
<td>N$_2$</td>
<td>1.8 ± 0.5</td>
<td>1.3 ± 0.1</td>
</tr>
<tr>
<td>O$_2$</td>
<td>1.7 ± 0.2</td>
<td>1.8 ± 0.2</td>
</tr>
<tr>
<td>CH$_3$NO$_2$</td>
<td>4.9 ± 0.4</td>
<td>5.1 ± 0.4</td>
</tr>
</tbody>
</table>

$^3$Normalized to helium values.

tremely efficient $^1A_u$ 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 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 $^3A_u$ 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 \(^{1}\text{A}_\text{u}\) 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 \(^{1}\text{A}_\text{u}\) glyoxal, the branching ratios are independent of collision partner. Since the apparent limit for quenching efficiency of the \(^{1}\text{A}_\text{g}\) state suggests that relaxation is dependent on the excited \(^{1}\text{A}_\text{g}\) levels, the second possibility cannot be immediately discarded. For example, if some excited rovibrionic levels are intramolecularly coupled to the \(^{3}\text{A}_\text{g}\) state and others to the \(^{1}\text{A}_\text{g}\) or other state, the external perturbation (collision) might quench the \(^{1}\text{A}_\text{g}\) 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 \(^{3}\text{A}_\text{g}\) glyoxal loss are photochemical decomposition and internal conversion to the \(^{1}\text{A}_\text{g}\) ground state. There is no evidence for significant photochemistry following excitation of the \(^{1}\text{A}_\text{g}\) state near the vibrationless level. Also, it has been established that photochemistry from higher vibrational levels follows intersystem crossing to the \(^{3}\text{A}_\text{g}\) state. Therefore photochemistry is ruled out as an independent channel.

The density of \(^{1}\text{A}_\text{u}\) states at the energy of the optically populated \(^{3}\text{A}_\text{g}\) levels is high enough \((\sim 10^{-6} - 10^{-8} \text{ cm}^{-1})\) that the statistical limit is expected to apply. In this case there would be no collisional dependence on the internal conversion rate. Lifetime data \(^{15}\) for many vibronic levels of the \(^{3}\text{A}_\text{g}\) 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 \(^{3}\text{A}_\text{g}\) state is the only important channel for collisional quenching of the \(^{1}\text{A}_\text{g}\) state. This conclusion agrees with the earlier work of Anderson et al. \(^{8}\).

V. PHOSPHORESCENCE FOLLOWING EXCITATION OF THE \(^{1}\text{A}_\text{g}\) STATE AT LOW PRESSURE

In the study of a similar molecule, biacetyl, it was found that there is substantial intramolecular intersystem crossing to the \(^{3}\text{A}_\text{g}\) state from the \(^{1}\text{A}_\text{g}\) state. The crossing was attributed to the presence of the \(^{3}\text{B}_\text{u}\) state, which may lie much higher in energy in glyoxal than in biacetyl. It is also predicted that vibrations with \(b\) 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 oscilloscope, 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 \(\mu\text{sec}\) decays intramolecularly long before any collisions occur. In the case of glyoxal, a phosphorescence signal can be observed exciting either the 0–0 or 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, \(^{1}\) the \(^{1}\text{A}_\text{g}\) 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 \(^{1}\text{A}_\text{u}\) state, characterized by some short lived emission and rapid vibrational relaxation to low-lying levels of the \(^{1}\text{A}_\text{g}\) 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 \(\nu_8\), the only \(b\) 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 \(^{1}\text{A}_\text{g}\) state of glyoxal has been studied for 24 collision partners with quenching cross sections in the range 1.3–22 \(\text{Å}^2\). 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 \(^{1}\text{A}_\text{g}\) 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 \(^{1}\text{A}_\text{g}\) state. This observation is interpreted as an indication that not all populated rovibrionic levels of the \(^{1}\text{A}_\text{g}\) state are coupled equally well with \(^{3}\text{A}_\text{g}\) 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 $1A_u - 3A_u$ 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 $1A_u$ state from the $3A_u$ 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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