Energy transfer in the $^{1}A_u$ state of glyoxal. III. Deuterium effects

P. F. Zittel and W. C. Lineberger

Department of Chemistry, University of Colorado
and Joint Institute for Laboratory Astrophysics, University of Colorado and National Bureau of Standards,
Boulder, Colorado 80309

(Received 26 November 1976)

Collision-free lifetimes and collisional quenching rate constants are reported for a number of single vibrational levels of glyoxal-\(d_1\) ($^{1}A_u$) and glyoxal-\(hd\) ($A^+$) and are compared with previous results for glyoxal-\(h_2\). There was some success in correlating the dependences of collision-free decay rates on specific vibrational level and on isotopic substitution with the predictions of intramolecular, nonradiative decay theory. There are strong isotope effects on the collision-free lifetimes, but the rate constants for collision deactivation of a vibrionic level, which increase sharply with energy in the excited state, are strikingly isotope independent. The increase is believed to be primarily a result of increased intersystem crossing rate and is compared with a mixed state model proposed by Freed.

I. INTRODUCTION

The application of narrow-band excitation and observation techniques to the study of intramolecular radiationless transitions in polyatomic molecules has produced a wealth of data, detailing the dependence of collision-free radiationless decay processes on the vibrational energy and symmetry of specifically excited vibronic states. Both internal conversion (IC) and intersystem crossing (ISC) processes have been studied, and in some cases the effect of isotopic substitution has been assessed. Such detailed data provide a severe test for detailed theories of intramolecular radiationless processes. In cases where intramolecular collisions open new pathways for radiationless decay and vibrational relaxation, measurements of the dependence of these quenching processes on the nature of vibronic states and on collision partners have also been made. Recent theories have attempted to describe the mechanisms for collisionally induced quenching.

Radiationless transitions have been studied for small, intermediate, and large molecules. Yeung and Moore\(^1\) and Miller and Lee\(^2\) have detailed the vibronic level dependence of collision-free radiationless decay of formaldehyde and its singly and doubly deuterated isotopomers. The radiationless rates were compared with the results of detailed theoretical calculations\(^3\) based on the models of Lin\(^4\) and of Chock, Jortner, and Rice.\(^5\) Thayer, Pocius, and Yardley\(^6\) have studied the intramolecular decay of specific vibronic levels of the six-molecule propylene, concluding that both IC and ISC occur in the absence of collisions. Detailed theoretical calculations of the rates for both radiationless processes were made as a function of vibronic level. Radiationless transitions of single vibronic levels of acetic acid,\(^7\) biacetyl,\(^8,9\) and substituted 1,2,4-triazoline-3,5-diones\(^10\) have also been studied. Extensive studies of the effect of isotopic substitution on the radiationless decay of single vibronic levels of benzene,\(^11-13\) naphthalene,\(^14-17\) styrene,\(^18\) pyrazine,\(^19\) and aniline\(^19\) have been reported. The dependence of decay rates on the nature of the initially excited vibrational mode and on isotopic substitution has been compared with theory in some cases,\(^12,13,20,21\)

Like other small and intermediate sized molecules, glyoxal, (CHO)\(2\), presents opportunities for studying a wealth of radiationless decay processes. In the absence of collisions, electronically excited $^{1}A_u$ glyoxal ($E = 22,000 \text{ cm}^{-1}$) decays nonradiatively, probably to highly vibrationally excited levels of the ground $^{1}A_g$ state.\(^22,23\) Collision-free decay to the $^{3}A_u$ state, lying ~3000 cm\(^{-1}\) below the $^{1}A_u$, is thought not to occur because of the low density of triplet levels (~3/cm\(^{-1}\) in the region of the $^{1}A_u$ origin). In contrast, collisional quenching of the $^{3}A_u$ state produces the $^{1}A_u$ state with nearly unit quantum yield.\(^24,25\) Collisional vibrational relaxation within the $^{1}A_u$ manifold competes with ISC and has been observed in some levels of glyoxal.\(^26,27\) As the excess energy in the $^{1}A_u$ state is increased above ~2500 cm\(^{-1}\), rapid biexponential decay is observed,\(^28\) apparently as a result of strong vibronic singlet-triplet mixing.

In an earlier paper, Beyer et al.\(^22\) presented collision-free decay rates and collisional quenching rate constants for single vibronic levels of glyoxal-\(h_2\). We present here analogous results for single vibronic levels of glyoxal-\(hd\) and glyoxal-\(d_2\). Extensive spectroscopic\(^29-32\) and normal coordinate\(^29,33\) analyses have assigned the $^{1}A_g$-\(^1\)A\(^\prime\)-\(^1\)A\(^\prime\) absorption spectra of glyoxal-\(d_2\) and glyoxal-\(hd\), making possible the identification and excitation of specific vibrational levels of the excited electronic state. The isotope effects on collision-free decay rates and on collisional quenching rates are quite different and should provide additional tests of radiationless decay theories.

II. EXPERIMENTAL

The apparatus used for the experiments reported here has been described in detail previously.\(^22\) In brief, an Nd laser pumped dye laser is used to excite specific vibrational levels of \(A_u\) glyoxal-\(d_2\), or \(A^\prime\) glyoxal-\(hd\). The dye laser output is 0.1-0.3 mJ/pulse in pulses of ~10\(^{-6}\) sec duration. The 0.5-1.0 Å bandwidth is adequately narrow to excite single vibronic levels of the \(^{1}A_u\) \((A^\prime)\) electronic state. Fluorescence is viewed at right angles to the path of the laser beam through a
monochromator with slits set to give a 10 Å bandpass. The Å bandpass ensures observation of an entire vibronic emission band, and effects of rotational relaxation are thus suppressed. The light passing through the spectrometer is detected by an RCA 8575 photomultiplier, amplified, and recorded on a Biomation 610 transient recorder. The digitized data are read into a PDP8/E computer, and the data from several hundred laser pulses are summed coherently to produce a decay curve with very high S/N. Exponential decay times, determined from a least-squares fit to decay curves for at least three lifetimes, are easily determined to ± 1%.

The gas handling system used here is identical to the system used previously with glyoxal-\(h_2\). A slightly different fluorescence cell and optical arrangement were used for the glyoxal-\(d_2\) and glyoxal-\(hd\) experiments. Since the collision-free lifetimes of the glyoxal-\(d_2\) levels are ~10 µsec (five times longer than the typical glyoxal-\(h_2\) lifetime), we utilized a larger fluorescence cell and viewing region than were used in the earlier glyoxal-\(h_2\) experiments. The fluorescence cell was a Pyrex cross with sapphire windows. The diameter of the cylindrical elements of the cross was 5 cm, and the viewing region was 3.5 cm in the smallest dimension. At very low pressures, where the mean free path is larger than the cell dimensions, less than 1% of the initially excited glyoxal molecules have left the viewing region after 30 µsec (i.e., three collision-free lifetimes of glyoxal-\(d_2\)). All glyoxal-\(d_2\) and glyoxal-\(hd\) lifetimes reported here were measured in the fluorescence cell described above. As a check, some lifetimes were measured again in the fluorescence cell originally used for glyoxal-\(h_2\), which has a viewing region of ~1 cm. Glyoxal-\(hd\) lifetimes were identical in both cells. Glyoxal-\(d_2\) lifetimes were very slightly shorter in the smaller cell at the lowest pressures. For measurements of the lifetimes of some combination levels reached via weak absorptions, a multiple-pass arrangement was used to increase S/N. The laser beam was passed through the cell five times in a horizontal plane between mirrors at the ends of the fluorescence cell. Lifetimes measured with both single- and multiple-pass arrangements were identical.

Glyoxal-\(hd\) and -\(d_2\) were synthesized by exciting ethylene-1, 1-\(d_2\) and ethylene-\(d_4\), respectively, with selenium dioxide in the presence of phosphorous pentoxide at ~200 °C. The ethylene isotopes were purchased from Merck, Sharpe, and Dohme of Canada, and stated isotopic purities were 98% and 99%, respectively. The glyoxal was purified by trap-to-trap distillation and stored at dry ice temperature. The visible absorption spectra of the three isotopes (Fig. 1) were recorded on

![Graph](image-url)
a Cary 14 spectrometer. The absorption spectra and subsequent fluorescence experiments, described in Sec. IIIA, confirmed the isotopic purity of the samples.

III. RESULTS

A. Absorption spectra

The visible absorption spectra of the three glyoxal isotopes displayed in Fig. 1 are quite similar. The same allowed absorption peaks occur for all three isotopes with nearly identical integrated intensities and are shifted slightly by isotope shifts of the vibrational frequencies. The vibronically allowed transitions involving the $v_6$ vibrational mode (CH wag) appear with similar intensities in all three spectra and comprise ~15% of the total absorption. Only $v_5$ has the proper symmetry ($b_2$) to vibronically couple the $1A_u$ and $1A_g$ states of glyoxal-$h_0$ or $-d_0$ in a radiative transition. The lower symmetry of glyoxal-$hd$ permits additional allowed and vibronically allowed transitions, but none appears in the spectrum. One band, $5^1T_1$, has a somewhat larger absorption in glyoxal-$hd$ than in either of the other isotopes. The $8^1$ and $5^1T_1$ levels of glyoxal-$hd$ are nearly isoenergetic and have the correct symmetry in the $C_2$ point group to mix through Fermi or Coriolis interactions. Fermi and Coriolis mixing has been observed between various vibrations in the ground electronic state for all three isotopes. Thus, the $8^1$ and $5^1T_1$ levels of glyoxal-$hd$ may not be completely separable. Laser excitation on the $8^1$ and $5^1T_1$ absorptions gave small amounts of fluorescence which appeared to originate from the $5^1T_1$ and $8^1$ levels, respectively. This was not the case for the glyoxal-$h_0$ and glyoxal-$d_0$ isotopes, where symmetry forbids mixing of $8^1$ and $5^1T_1$ levels.

The nearly identical integrated absorptions for the three isotopes lead to nearly identical estimates of the radiative lifetimes. Anderson$^{23}$ estimates $\tau \approx 10$ μsec for glyoxal-$hd$. Vibronic shortening of the $8^1$ lifetime and lifetimes of combination levels involving $v_6$ should be similar for the three isotopes, since the $8^1$ absorptions indicate similar vibronic coupling on this band for all isotopes.

The locations of several absorptions to combination levels ($8^12^1$, $8^14^1$, $8^15^1$, and $2^15^1$) of $1A_u$ glyoxal-$d_0$ have not been previously given. We assigned the absorptions indicated in Fig. 1 on the basis of the vibrational energies of the fundamentals. The assignments were confirmed by assigning the bands of the fluorescence spectrum of a particular combination level to a multitude of hot bands, originating unambiguously from the excited combination level. Figure 2 shows the fluores-
cence spectrum resulting from excitation of the $8^12^1$ combination level of glyoxal-$d_2$. All strong fluorescence bands are assigned easily to hot bands originating from $8^12^1$. The fluorescence decay times are identical for each of the strong bands. It should be noted that at a pressure of 11 mtorr, where 80% of the fluorescence decay rate is due to collisional quenching, no strong fluorescence appears on bands originating from other vibrational levels of the $^1A_g$ state (i.e., $8^12^17^1$, $8^12^12^1$, $5^1$, etc.). Some fluorescence does appear at the position of the 0-0 band, but this may also be reasonably assigned to hot bands originating from the $8^12^1$ level.

B. Isotopic purity

The intensities of the shifted absorption peaks in the visible absorption spectra of the three isotopes show that the samples are fairly isotopically clean. In particular, the 0-0 and $8^1$ absorption bands are shifted as predicted for the isotopes, and identifiable amounts of isotopic contamination are not seen. The presence of underlying, unresolved absorption makes a precise estimate of isotopic purity from the absorption spectra impossible.

A precise estimate was possible through a series of fluorescence experiments. The laser was tuned to the peak of the 0-0 absorption of a particular isotope, and the fluorescence on the $8^1$ emission band was integrated over a set number of laser pulses with a sample-and-hold integrator. The cell was then evacuated and filled to the same pressure with a different isotope, and integrated fluorescence was again measured on the $8^1$ band of the first isotope. Because of the large isotope shift of the $8^1$ emission, the $8^1$ fluorescence from the various isotopes is almost completely separated. The relative fluorescence yields of the two consecutive experiments set limits on the fraction of the first isotope contained in the sample of the second isotope. A series of experiments set an upper limit of <2.5% impurity of glyoxal-$d_2$ in the glyoxal-$hd$ sample and <4% glyoxal-$h_2$, or glyoxal-$hd$, in the glyoxal-$d_2$ sample. Overlapping glyoxal-$hd$, emission bands did not allow a precise upper limit to be set on glyoxal-$h_2$ in the glyoxal-$hd$ sample, but it is probably at the few percent level. Since the fluorescence bands from two isotopes are not perfectly separated, the upper limits on isotopic impurities quoted above may be pessimistic. It was also confirmed that the glyoxal-$hd$ sample did not isotopically exchange while kept at dry ice temperature during the several-week course of the experiments. If present, small amounts of isotopic impurity do not affect zero-pressure lifetime measurements for a particular isotope, since isotopic shifts of absorption and emission bands allow isotopes to be excited selectively. Quenching rate constants would be affected significantly only if the self-quenching rate for the excited isotope is more than an order of magnitude lower than quenching by the other isotopes. It is shown below that quenching rates are practically independent of isotopic substitution.

C. Lifetimes and quenching rate constants

Fluorescence decay rates were measured for a variety of vibrational levels of glyoxal-$hd$ and $-d_2$, as a function of glyoxal pressure. Plots of decay rate against pressure gave straight lines with intercept $k_{sp}$ and slope $k_r$. The quantity $k_{sp}$ is the zero-pressure decay rate, due to radiative and intramolecular nonradiative decay in the absence of collisions. The values of $k_{sp}$ determined for vibrational levels of $^1A^*$ glyoxal-$hd$ and $^1A_g$ glyoxal-$d_2$ are plotted in Figs. 3 and 4, respectively. In addition, $1/k_{sp}$, the zero-pressure lifetimes, are listed in Tables I and II. The relative contributions of radiative processes to $k_{sp}$ will be discussed in Sec. IV.

A criterion for deciding that predominantly single vibronic level excitation had been achieved was that the features of the fluorescence spectrum at low pressure be assignable to the excited level. Under these conditions, the observed decays were single exponentials over at least three decades. These data (Figs. 3 and 4) extend up to 2000 cm$^{-1}$ excess energy in the $^1A_g(^1A^*)$ state.
TABLE I. Collision-free lifetimes and quenching rate constants for individual vibronic levels of the \(^{1}A''\) state of glyoxal-hd.

<table>
<thead>
<tr>
<th>(^{1}A'') Level</th>
<th>Wavelength ((\AA)) (^{4})</th>
<th>Excite (Band) Observe (Band)</th>
<th>Lifetime (nsec)</th>
<th>Quenching rate constant (10(^{-10}) cm(^3) sec(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>4427 (0-0)</td>
<td>4792 (5)</td>
<td>4.41 \pm 0.08(^{5})</td>
<td>1.83 \pm 0.25(^{5})</td>
</tr>
<tr>
<td>7(^{1})</td>
<td>4526 (7)</td>
<td>4729 (6)</td>
<td>4.36 \pm 0.03</td>
<td>3.9 \pm 0.3</td>
</tr>
<tr>
<td>7(^{1})</td>
<td>4596 (7)</td>
<td>4716 (6)</td>
<td>4.42 \pm 0.04</td>
<td>6.1 \pm 0.3</td>
</tr>
<tr>
<td>7(^{1})</td>
<td>4486 (7)</td>
<td>4696 (6)</td>
<td>4.20 \pm 0.11</td>
<td>6.4 \pm 0.8</td>
</tr>
<tr>
<td>5(^{1})</td>
<td>4445 (5)</td>
<td>4555 (5)</td>
<td>3.85 \pm 0.03</td>
<td>3.8 \pm 0.3</td>
</tr>
<tr>
<td>5(^{1})</td>
<td>4400 (5)</td>
<td>4604 (5)</td>
<td>2.50 \pm 0.03</td>
<td>5.9 \pm 0.6</td>
</tr>
<tr>
<td>6(^{1})</td>
<td>4381 (6)</td>
<td>4583 (6)</td>
<td>2.86 \pm 0.03</td>
<td>7.0 \pm 0.5</td>
</tr>
</tbody>
</table>

\(^{1}\)Wavelengths are \(\pm 1 \AA\); excitation bandwidth is \(1 \AA\); observation bandwidth is \(10 \AA\).
\(^{2}\)Errors are due to standard deviations of the least-squares fit.

Recently van der Werf et al. reported observation of biexponential decay in glyoxal\(^{28}\) and biacetyl.\(^{9}\) The observations were interpreted as evidence for reversible intersystem crossing and appear qualitatively consistent with a theory of that process.\(^{25}\) Yardley and co-workers\(^{1}\) have observed similar behavior in the “intermediate” methylyglyoxal molecule. All glyoxal data reported here are below the region in the \(^{1}A_{u}(^{1}A'')\) manifold where biexponential decay is first seen,\(^{28}\) and in particular such decay is not observed by us.

The quenching rate constants \(k_{q}\) were determined over the pressure range 0.5-5.0 mtorr. At the highest pressures \(k_{tp}\) is generally less than \(k_{sp}\), and vibrational equilibration effects\(^{28}\) on the fluorescence decay curves, which are important for torsional vibrations at higher pressure, are not important in these measurements. All fluorescence decays were single exponentials over three decades of decay, and all Stern-Volmer plots were linear. The quantity \(k_{q}\) includes all processes which collisionally \textit{depopulate} an initially excited level

\[ k_{q} = k_{IC} + k_{ISC} + k_{VIB} \]

(1)

where \(k_{IC}, k_{ISC},\) and \(k_{VIB}\) are the rate constants for collisionally induced internal conversion, intersystem crossing, and vibrational relaxation, respectively. Arguments for the relative importance of the terms in Eq. (1) will be presented in Sec. IV. The measured values of \(k_{q}\) for various levels of \(^{1}A''\) glyoxal-hd and \(^{1}A_{u}\) glyoxal-d\(_{2}\) are plotted in Figs. 5 and 6 and are listed in Tables I and II, respectively.

### IV. DISCUSSION

#### A. Zero-pressure decay rates

1. Radiative and nonradiative contributions to \(k_{tp}\)

The zero-pressure decay rates for specific levels of \(^{1}A_{u}(^{1}A'')\) glyoxal, listed in Tables I and II and Ref. 22, are the sum of all radiative and nonradiative decay rates for the isolated molecule. Without measurements of fluorescence quantum yields, it is difficult to determine separately the dependence of \(k_{q}\) and \(k_{nr}\) on vibrational level. A comparison of zero-pressure decay rates for the three isotopes and an assessment of the importance of vibronically induced, radiative decay do, however, allow one to interpret much of the zero-pressure decay data in terms of either radiative or nonradiative effects.

There is undoubtedly some dependence of \(k_{q}\) on vibrational level, particularly for levels involving the \(v_{b}\)
(CH wag) vibration, which has the proper symmetry to vibronically couple the $^1A_g$ and $^1A_u$ electronic states.\cite{26,27} For glyoxal-hd, $v_6$ (CH wag) and $v_9$ (torsion) may also vibronically couple the $^1A_g$ and $^3A_u$ states; however, no evidence for such coupling is seen. In the absorption spectra (Fig. 1) one observes significant absorption on the vibronically induced $\delta v$ and $\delta v^*$ transitions, which is $\approx 15\%$ of the total absorption. Although the $^1B_1$ level and $^1B_2^m$ combination levels have additional, vibronically allowed, radiative decay pathways (i.e., $\delta v^2$ and $\delta v^2$), it seems unlikely that vibronically induced contributions to the radiative decay rate are larger than the radiative decay rate due to allowed transitions. The potential effect of vibronically induced shortening of radiative lifetimes on $k_{sp}$ depends upon the relative importance of radiative and nonradiative contributions to $k_{sp}$ and is quite different for the three glyoxal isotopes. The effect for each isotope is considered in the following discussion.

A comparison of pressure-free decay rates for the fundamental vibronic levels of the three glyoxal isotopes is made in Fig. 7. The dependence of $k_{sp}$ on isotopic substitution and excess vibrational energy suggests some conclusions about the relative contributions of $k_p$ and $k_{sp}$ to the decay of the different isotopes. The radiative lifetime of glyoxal-$h_2$ is estimated to be $\approx 10$ \mu s.\cite{24} The nearly identical integrated absorptions for the $^1A_g - ^3A_u$ transition of the three isotopes suggest nearly identical radiative lifetimes. While $k_{sp}$ for most glyoxal-$d_2$ levels is close to the estimated radiative lifetime, $k_{sp}$ for glyoxal-$h_2$ and -hd levels is considerably larger and due in large part to nonradiative decay. For glyoxal-$d_2$ levels (with the exception of $^1B_1^m$ and $^1B_2^m$ levels) are nearly identical ($\approx 10$ \mu s). If the levels of glyoxal are reasonably well described by the Born–Oppenheimer picture, and vibronically induced radiative decay from levels which do not have the active promoting mode ($v_9$) excited is about the same, then one expects little variation in $k_{sp}$ for these vibrational levels. The variation of $k_{sp}$ with vibrational energy seen for glyoxal-$h_2$ and -hd is not apparent for glyoxal-$d_2$, probably because $k_{sp}$ is primarily radiative for glyoxal-$d_2$, $k_{sp}$ for the $^1B_1^m$ and $^1B_2^m$ combination levels of glyoxal-$d_2$ is, in the worst case, $40\%$ larger than $k_{sp}$ for the vibrationless level. Since $k_{sp}$ for the vibrationless level is primarily radiative, one cannot rule out the possibility that the modest increase in $k_{sp}$ for the $^1B_1^m$ level and $^1B_2^m$ combination level is to a large degree radiative and vibronically induced in nature for glyoxal-$d_2$. In contrast to glyoxal-$d_2$, the zero pressure decay rates for glyoxal-$h_2$ are approximately four times larger than the estimated radiative decay rate, or the decay rate observed for glyoxal-$d_2$. The $k_{sp}$ for levels which do not have $v_9$ excited show an increase with increasing vibrational energy. Both results indicate collision-free decay of glyoxal-$h_2$ is primarily nonradiative. The enhancement of $k_{sp}$ for $^1B_1^m$ and $^1B_2^m$ combination level is also much larger than for glyoxal-$d_2$. Since, for glyoxal-$h_2$, the
decay rate for the $8^1$ level is 2.8 times larger than the rate for the vibrationless level, and since $k_{sp}$ for the vibrationless level is essentially nonradiative, one concludes that the increase in $k_{sp}$ for the $8^1$ and $8^1X^b$ levels of glyoxal-$h_2$ is essentially nonradiative in nature.

The zero-pressure decay rates for glyoxal-$h_2d_4$ lie between the results for glyoxal-$h_2$ and glyoxal-$d_2$. The decay rates for symmetric vibrational levels show some dependence on vibrational energy and are a factor of 2 larger than the estimated radiative decay rate. Thus, $k_{sp}$ for glyoxal-$h_2d_4$ includes substantial (probably > 50%) nonradiative contributions, but cannot be considered almost totally nonradiative, as is the case for glyoxal-$h_2$. $k_{sp}$ for the $8^1$ level is only 76% larger than $k_{sp}$ for the vibrationless level, and again one cannot assign this as a totally nonradiative effect.

If one assumes that the radiative lifetimes of the vibrationless level of the $1A^1(I_A^1)$ state are approximately equal for the three isotopes, and in the range $10-20$ μsec, one can determine limits for the nonradiative contributions to $k_{sp}$ for the vibrationless level of the three isotopes: 0.88 $k_{sp}(h_2) \geq k_{sp}(h_2) \geq 0.76$, 0.78 $k_{sp}(h_d) \geq k_{sp}(h_d) \geq 0.56$, and 0.50 $k_{sp}(d_2) \geq k_{sp}(d_2)$. The ratios of nonradiative decay rates may also be determined: $2.9 = k_{sp}(h_2)/k_{sp}(h_d) \geq 1.7$ and $k_{sp}(h_d)/k_{sp}(d_2) \geq 6.0$. In the following discussion, we consider the zero-pressure decay rates and vibrionic level effects for glyoxal-$h_2$ to be essentially nonradiative, including the anomalous increase in $k_{sp}$ for the $8^1$ and $8^1X^b$ combination levels. These decay rates are discussed in terms of nonradiative decay theory. For glyoxal-$d_2$, the possibility is considered that anomalous values of $k_{sp}$ for the $8^1$ and $8^1X^b$ levels may be substantially radiative in nature.

2. Theoretical background

The commonly used models for nonradiative decay in isolated molecules are formulated in terms of transitions between initial and final Born–Oppenheimer (BO) states connected by a nuclear kinetic energy perturbation.\(^4\) The nonradiative decay rate from an initial vibrionic state $|s, i\rangle$ to all final levels $|l, j\rangle$ of a different electronic state is written as

$$k_{nr}(s, i) = \frac{2\pi}{\hbar} \sum_j \left| \sum_{k=1}^b C_{s,i}^b Q_k^s \right|^2 \left\langle \frac{\partial}{\partial Q_k} | m_k^i \rangle \right\rangle \left\langle \delta(E_{s,i} - E_{s,j}) \right\rangle,$$

where $s$ and $l$ designate initial and final BO electronic states, $i$ is the initial vibrational state with $n_k^i$ quanta of mode $x$ excited; $j$ is the final vibrational state with $m_k^j$ quanta of mode $x$ excited. For the case of internal conversion, $C_{s,i}^b$ is given by

$$C_{s,i}^b = \frac{R}{i} \left\langle \left| \frac{\partial}{\partial Q_k} | s, i\rangle \right| \right\rangle \approx \frac{R}{i} \left\langle s, l \left| (\nabla V/\partial Q_k)|i\rangle \right. \right\rangle \frac{1}{E_l - E_s},$$

where $Q_k$ is a BO electronic wave function and $V$ is the potential energy between electrons and nuclei. The modes $Q_k$ which have the proper symmetry to couple the initial and final electronic states are termed promoting modes. (For glyoxal-$h_2$ and $d_2$, $\nu_6$ and $\nu_9$ are the only promoting modes, while for glyoxal-$h_d$, symmetry also allows $\nu_7$.) The initially excited vibrational mode, for which $n_k^j \neq 0$, is termed the optical mode $a$ and for convenience is separated from the final product of Franck–Condon factors over the remaining vibrational modes. The modes which are most efficiently excited in the final electronic state (i.e., $n_k^j > n_k^s$) are termed accepting modes. Generally, the accepting modes are high frequency symmetric stretching modes or involve significant changes in frequency and equilibrium geometry between the initial and final electronic states. Equation (2) may be written in a simplified, phenomenological form

$$k_{nr} \approx 2\pi \frac{V^2}{\hbar},$$

where $V$ is termed an "effective" Franck–Condon factor and $\rho$ is an "effective" density of final vibronic levels.

Equation (2), or derivative versions, has been used to calculate absolute internal conversion rates for specific vibronic levels of formaldehyde\(^5\) and propynal.\(^6\) A second-order perturbation version has been applied to intersystem crossing in propynal.\(^6\) These calculations have met with mixed success, roughly reproducing the magnitude and general vibrational energy dependence of decay rates, but failing to reproduce the detailed dependence on specific vibrational levels. Calculations of isotope effects for formaldehyde are reasonably close to observation. Calculations of relative decay rates for larger molecules\(^20,\) have been successful in describing the detailed dependence on specific, initial vibronic level, having utilized adjustable parameters to describe the vibrational modes of the final electronic state.

Some of the general conclusions of these previous studies will be applied to the glyoxal nonradiative decay process.

3. Application to glyoxal

The Franck–Condon factors in Eq. (2) are largest for small changes in vibrational quantum numbers. The largest contributions to $k_{nr}$ should occur when high frequency modes (i.e., C-H stretching modes) accept the excess energy. Deuteration of the accepting modes requires larger quantum number changes upon nonradiative decay, and consequently smaller Franck–Condon factors with generally decreased nonradiative decay rates. This "normal" isotope effect is large for formaldehyde\(^1,2\) $k_{nr}(h_2)/k_{nr}(d_2) > 20$, where nonradiative decay probably (although not conclusively) involves IC with a large energy gap. Calculations of the isotope effect on IC in formaldehyde are in reasonable agreement with the observed effect. The isotope effect is considerably smaller (ratio of 2) for larger molecules\(^13,14,20\) where the nonradiative decay is ISC to a final electronic state lying much closer in energy to the initial state. In highly vibrationally excited levels of some large molecules, where IC is thought to compete with ISC, isotope
effects can be larger. The isotope effect for glyoxal is substantial. Assuming radiative lifetimes in the range 10–20 μsec for the vibrationless level of the three glyoxal isotopes, the nonradiative decay rates for the vibrationless level are in the ratios 2.9 ≈ k_{nr}(h2)/k_{nr}(hd) ≈ 1.8 and k_{nr}(h2)/k_{nr}(d2) ≈ 6.0. Such a large isotope effect would seem to be characteristic of internal conversion (IC), involving large energy gaps.

In a simplified picture [Eq. (3)], k_{nr} may be thought of as the product of an "effective" Franck–Condon (FC) factor and an "effective" density of final vibrational levels. The broad dependence of k_{nr} on excess vibrational energy should parallel the broad dependence of the FC factors and level density on energy, and in general k_{nr} increases with increasing vibrational excitation of the initial state. In formaldehyde, Yeung and Moore\(^6\) found that k_{nr} increased much faster than the density of isoenergetic 1A_1 vibrational levels and attributed the increase to Franck–Condon factors, increasing substantially with increasing vibrational energy. For propynal both IC and ISC apparently occur in the absence of collisions, and the increases in both IC and ISC rates (factors of 3 and 10 for 1500 cm\(^{-1}\) of excess energy for IC and ISC, respectively) roughly parallel the increasing density of ground and triplet vibrational densities, respectively. For glyoxal-h\(_2\), where the zero-pressure decay rate is primarily nonradiative, the decay rate increases slowly with excess vibrational energy, roughly paralleling the density of 1A_1 vibrational levels (Fig. 7). Since glyoxal-h\(_2\) and propynal are quite similar in terms of the energy gaps and vibrational level densities, the close parallel between decay rate and 1A_1 level density for glyoxal-h\(_2\) supports the conclusion that the nonradiative decay in glyoxal-h\(_2\) is internal conversion. It is interesting that collision-free ISC does not seem to occur for glyoxal,\(^{52,23}\) while for propynal both IC and ISC occur with similar rates. The 1A_1 (′A′) level densities of glyoxal-d\(_2\) and −hd have very nearly the same energy dependence as the glyoxal-h\(_2\) level density. The shallower dependence of zero-pressure decay rates on vibrational energy for the symmetric vibrational levels (6\(^1\), 4\(^2\), 2\(^1\)) of glyoxal-hd and −d\(_2\) suggests that the decays of these isotopes are due in larger part to radiative decay, which is probably not strongly dependent on vibrational state for the symmetric vibrations.

Although the nonradiative decay rates of glyoxal-h\(_2\) generally parallel the 1A_1 density of states, there is considerable dependence on specific vibrational level. In particular, k_{nr} for the 8\(^1\) and 8X\(^6\) combination levels are anomalously large, and decay rates for 9\(^1\) levels show little dependence on excess vibrational energy. Although the extended calculations of k_{nr} for formaldehyde\(^3\) and propynal\(^8\) have not reproduced the dependence of k_{nr} on specific vibrational level, simpler calculations of relative decay rates have suggested some qualitative relationships between k_{nr} and the nature of the optically excited vibrational level. In applying a version of Eq. (2) to ISC in benzene, Heller et al.,\(^21\) have noted the strong influence of the Franck–Condon factors for the optically excited vibration on k_{nr}. If ν\(^2\)/ν\(^1\) < 1, where ν\(^1\) and ν\(^2\) are the frequencies of the optically excited vibrational mode in the initial and final electronic states, k_{nr} increases as mode ν becomes excited because mode ν becomes an increasingly better accepting mode. If ν\(^2\)/ν\(^1\) ≥ 1, k_{nr} generally decreases or remains constant with increasing excitation of mode ν. In a qualitative sense, the glyoxal-h\(_2\) results for the ν\(_4\) and ν\(_5\) levels parallel these trends, since ν\(^4\)(A\(_2\))/ν\(^4\)(A\(_1\)) = 1.84 and ν\(^5\)(A\(_2\))/ν\(^5\)(A\(_1\)) = 0.69. Thus, the anomalous decay rates of the ν\(_5\) and ν\(_4\) levels may be due at least partially to the efficiency of those modes as accepting modes in the IC processes.

The possibility that part of the increase in k_{nr} for the 8\(^1\) level of all the isotopes is due to vibronic shortening of the radiative lifetime has been discussed earlier (Sec. IV.A.1). For glyoxal-h\(_2\) this may not be a significant effect; however, another nonradiative decay channel for 8\(^1\) is possible. The 8\(^1\) level has the proper symmetry (h\(_2\)) to couple intramolecularly the 1A_1 and 5A_1 states through a second-order, spin–orbit perturbation mechanism.\(^{36,37}\) Previously, collision-free ISC from the 8\(^1\) level has been discounted because of the sparse density of the triplet levels (∼10 cm\(^{-1}\)) isoenergetic with 8\(^1\) and because of the lack of phosphorescence\(^{40}\) following excitation of 8\(^1\) at low pressure (1 mtorr). Thayer and Yardley,\(^6\) however, have proposed ISC as an efficient collision-free decay process for propynal, where level densities are comparable to glyoxal. Anderson et al.,\(^23\) have deduced that vibrational levels of 1A_1 glyoxal which are isoenergetic with the 1A_1 8\(^1\) level undergo fast unimolecular decay with a decay rate comparable to the nonradiative decay rate of the 1A_1 levels. [If one uses Anderson’s value of (k_{TCS}) = 4 torr\(^{-1}\) and approximates (k_{ICS} + k_{TCS}) by the gas kinetic collision rate, then 1/k_{ICS}, the unimolecular lifetime, is ~0.7 μsec.] Fast, collision-free decay of vibrationally excited 1A_1 levels could preclude phosphorescence from levels created by ISC from 8\(^1\) levels of the 1A_1 state. We also note that magnetic rotation spectra show some intramolecular mixing of singlet and triplet states in the region of the 1A_1 8\(^1\) level. Although collision-free ISC from the 1A_1 8\(^1\) level to such a sparse triplet manifold seems unlikely, it should not be ruled out entirely.

Another interesting effect is evident for the collision-free decay of glyoxal-d\(_2\) combination levels involving ν\(_5\). Combinations of ν\(_5\) and increasingly energetic symmetric vibrations (ν\(_4\), ν\(_5\), and ν\(_3\)) decay with increasingly longer zero-pressure lifetimes (see Fig. 4). Whether this is the result of decreasing k_{nr}, or decreasing k_{nr} is not clear, although the effect is larger for glyoxal-d\(_2\) than for glyoxal-h\(_2\), where k_{nr} is less important. Theoretical treatments\(^2\) of combination levels involving an active and an inactive optical mode suggest that the nonradiative decay rate for the combination level should be at least as large as the decay rate for the optically excited active mode alone (i.e., ν\(_5\)). We have previously noted (Sec. IV.A.1) that the increase in k_{nr} for the glyoxal-d\(_2\) 8\(^1\) and 8X\(^6\) levels over the value of k_{nr} for the vibrationless level could be due primarily to vibronically induced radiative decay. The lengthening of radi-
ative lifetimes of levels, connected to the ground electronic state by vibronic interaction, upon addition of symmetric vibrations has been observed for formaldehyde.\textsuperscript{5} For formaldehyde the radiative lifetimes of the $4^2\Pi$ and $5^2\Pi$ levels increase dramatically as the number of quanta of the symmetric $\nu_2$ mode increases from 0 to 3 and 0 to 2, respectively. The increase in zero-pressure lifetimes for the $8^1\Sigma^+$, $8^3\Sigma^+$, $8^1\Sigma^+$, and $8^2\Sigma^+$ series in glyoxal-$d_2$ may similarly reflect a decrease in the vibronically induced part of the radiative decay rate upon addition of increasingly energetic symmetric vibrations to $8^1\Sigma^+$.\textsuperscript{5}

B. Quenching rate constants

The quenching rate constants listed in Tables I and II and Ref. 22 are the sum of all collisional rates which depopulate an initially excited vibronic level. Collisionally induced internal conversion to $^1A_2 (^1A')$, intersystem crossing to $^3A_1 (^3A'^*)$, and vibrational relaxation within the $^1A_1 (^1A'^*)$ manifold are included. Anderson\textit{et al.}\textsuperscript{25} and Beyer and Lineberger\textsuperscript{26} have deduced from relative phosphorescence quantum yields that electronic quenching of $^1A_1$ glyoxal-$h_2$ is almost entirely (>90%) ISC. It would appear that internal conversion is in the statistical limit and is not enhanced by collisions. The question of the relative contributions of ISC and vibrational relaxation to our single level quenching rate constants remains. For the analogous larger molecule, bicyclopropyl, vibrational relaxation apparently proceeds with cross sections larger than hard sphere.\textsuperscript{5} For the smaller molecule, formaldehyde, vibrational relaxation apparently has cross sections considerably smaller than hard sphere and is slower than collision induced electronic quenching for D$_2$CO.\textsuperscript{1} Vibrational relaxation cross sections have not been determined for HDCO or H$_2$CO. Beyer and Lineberger\textsuperscript{24} have measured an electronic quenching rate constant, $k_{\text{ISC}} = 0.63 \times 10^{10}$ cm$^3$/mol·sec, for vibrationally equilibrated $^1A_1$ glyoxal-$h_2$. This rate constant is a Boltzmann average of $k_{\text{ISC}}$ over low-lying vibrational levels, with the major contribution coming from the vibrationless and low-lying torsional ($\nu_2$) levels. If one assumes that $k_{\text{ISC}}$ is approximately the same for the vibrationless level and the lowest energy (233 cm$^{-1}$) $7^1\Sigma^+$ level and is equal to $k_{\text{ISC}}$, then the difference between our single level quenching rate constants and $k_{\text{ISC}}$ should be the vibrational relaxation rate constants $k_{\text{VIB}}$ for the 0 and $7^1\Sigma^+$ levels. With these approximations, one obtains $k_{\text{VIB}} \approx 1.2 \times 10^{10}$ and $3.9 \times 10^{10}$ cm$^3$/mol·sec for the 0 and $7^1\Sigma^+$ levels of glyoxal-$h_2$, respectively. These estimates are in excellent agreement with recently reported direct measurements of the electronic and vibrational quenching rate constants for the 0 and $7^1\Sigma^+$ levels.\textsuperscript{24} Single level quenching rate constants for the $7^1\Sigma^+$, $7^3\Pi$, and $7^1\Sigma^+$ levels of glyoxal-$h_2$ are nearly identical and only ~30% larger than the rate constant for $7^1\Sigma^+$, reflecting only a small increase in $k_{\text{ISC}}$ or $k_{\text{VIB}}$ for these levels.

The collisional quenching rate constants for the 0 and $7^1\Sigma^+$ levels of glyoxal-$d_2$ and $d_2$ are identical within experimental error to the rate constants for the analogous levels of glyoxal-$h_2$. The rate constants show a large difference between 0 and $7^1\Sigma^+$, a small difference between $7^1\Sigma^+$ and $7^3\Pi$, and approximately equal values for $7^3\Pi$ and $7^1\Sigma^+$. As in the case of glyoxal-$h_2$, the large increase in $k_{\text{VIB}}$ for the $7^1\Sigma^+$ levels over $k_{\text{ISC}}$ for the vibrationless level is probably due essentially to vibrational relaxation. One concludes that vibrational relaxation rate constants for the $7^1\Sigma^+$ levels of glyoxal-$hd$ and $d_2$ are approximately equal to the rate constants for glyoxal-$h_2$. Since vibrational “relaxation” of the vibrationless level must result primarily in excitation of the low frequency torsional levels, $k_{\text{VIB}}$ for the vibrationless level is related to $k_{\text{ISC}}$ for the torsional levels by Boltzmann factors, which are nearly identical for the relevant vibrations of the three isotopes. One concludes that $k_{\text{VIB}}$ for the vibrationless levels of glyoxal-$hd$ and $d_2$ is nearly the same as $k_{\text{VIB}}$ for glyoxal-$h_2$. Since the total quenching rate constants are identical for the vibrationless levels of the three isotopes, one therefore concludes that $k_{\text{ISC}}$ is approximately the same for the vibrationless level of all three isotopes and approximately equal to $k_{\text{ISC}}$.

Although vibrational relaxation of $\nu_2$ torsional levels is rapid (2–3 x gas kinetic), the relaxation rate constants do not appear to increase much with increasing vibration energy (compare $k_{\text{ISC}}$ for $7^1\Sigma^+$, $7^3\Pi$, $7^1\Sigma^+$, and $7^3\Pi$ for glyoxal-$h_2$). It also appears that the quenching rate constant, and thus the vibrational relaxation rate constant, for the fundamentals $\nu_2$ and $\nu_3$ are significantly smaller than the vibrational relaxation rate constants for roughly isoenergetic torsional levels (compare $k_{\text{ISC}}$ for $5^1\Sigma^+$ and $5^3\Pi$ for any of the isotopes). Thus, it is not obvious for levels above the vibrationless level that $k_{\text{VIB}}$ increases steeply with excess vibrational energy. We note in formaldehyde vibrational relaxation rate constants do not appear to increase substantially over 2500 cm$^{-1}$ of excess vibrational energy.\textsuperscript{1} Precise measurements of $k_{\text{VIB}}$ for glyoxal-$h_2$ levels other than the torsional levels have not been made. Photos and Atkinson\textsuperscript{28} have shown that some vibrational relaxation accompanies collisional quenching of the $5^1\Sigma^+$ level, but the relative values of $k_{\text{ISC}}$ and $k_{\text{VIB}}$ were not determined. Frad and Tramer\textsuperscript{28} concluded that resonant electronic energy transfer, leading to an apparent vibrational relaxation of the $8^1\Sigma^+$ level to the vibrationless level, proceeds with approximately a gas kinetic rate constant (~$2.5 \times 10^{10}$ cm$^3$/mol·sec), but Beyer\textsuperscript{27} measured a considerably smaller rate constant. Anderson\textit{et al.}\textsuperscript{25} concluded that 80% of the molecules excited to $^1A_1$ levels with ~1200 cm$^{-1}$ of vibrational energy are electronically quenched before being vibrationally relaxed to the vibrationless level of $^1A_1$. Our results for highly vibrationally excited levels indicate little fluorescence from levels other than the initially excited level at pressures where collisional relaxation is much faster than collision-free decay. Taking collisional relaxation of glyoxal-$d_2$ $^1A_1$ \textit{81}2\textit{1} as an example (Fig. 2), very little emission from levels other than the initially excited level is apparent, even though collisional relaxation accounts for more than 80% of the decay at 11 mtorr of pressure. Thus, it seems likely that vibrational relaxation occurs at gas kinetic collision rates for most levels (particularly within the manifold of $\nu_2$ torsional levels), but may not
account for the steep energy dependence or the large values of \( k_a \) (>6 x gas kinetic), for highly vibrationally excited levels. The rapid increase in \( k_a \) is probably due primarily to a rapid increase in electronic quenching (ISC), which eventually dominates \( k_a \) for high vibrational levels.

Collisional quenching rate constants for the fundamental vibrational levels of the three glyoxal isotopes are compared in Fig. 8. The nearly identical values of \( k_a \) for a particular vibrational level of all three isotopes are striking. With few exceptions the similarity extends to combination levels in this range of \( E_{\text{VIB}} \), which have been measured for more than one isotope. Above 1400 cm\(^{-1}\) of excess vibrational energy, no quenching rate constants have been measured for glyoxal-hd. Quenching rate constants for combination levels of glyoxal-h\(_2\) and glyoxal-d\(_2\) in the 1400–2200 cm\(^{-1}\) range rise steeply with \( E_{\text{VIB}} \) to a value equal to \( \sim 6 \times \) gas kinetic at 2100 cm\(^{-1}\) of excess vibrational energy. With one exception, 2\(^1\)\(^1\), identical levels in glyoxal-h\(_2\) and glyoxal-d\(_2\) again have nearly identical quenching rate constants. If, as we have suggested, \( k_a \) is predominantly electronic quenching in the region of high vibrational excitation and \( k_{\text{ISC}} \) for the vibrationless level is similar for all three isotopes, then \( k_{\text{ISC}} \) is remarkably isotope independent over a broad range of \( E_{\text{VIB}} \). In contrast to these results, Yeung and Moore\(^{1}\) found a large isotope effect on \( k_a \) for formaldehyde, paralleling the isotope effect on collision-free decay rates. Collisional quenching in formaldehyde may produce the same electronic state as collision-free decay and thus may involve the same intramolecular coupling. Glyoxal is quite different, since collisional and collision-free decay apparently produce different final electronic states. For glyoxal there is apparently little isotope effect on \( k_a \) and \( k_a \) increases much more rapidly with vibrational energy than does \( k_{\text{ ISC}} \).

Freed\(^{48}\) has proposed a mechanism for collision-induced ISC in intermediate-sized molecules which expresses the ISC rate as

\[
 k_{\text{ISC}} \approx n^2 k_{\text{relax}}
\]

where \( n \) is the number of triplet levels coupled intramolecularly to the initially excited singlet level, \( x^2 \)

\(<1 \) is a typical intramolecular coupling coefficient, and \( k_{\text{relax}} \) is a typical rotational, or vibrational, relaxation rate constant within the triplet manifold. If \( k_{\text{relax}} \) is relatively insensitive to excess vibrational energy, one would expect \( k_{\text{ISC}} \) to vary as a coupling coefficient (basically a Franck–Condon factor) times an effective density of triplet vibrational levels. Plotted in Fig. 6 are the collisional quenching rate constants and relative \( A_a \) vibronic level density \( \rho \) for glyoxal-d\(_2\). We note that \( k_a \) increases less rapidly than \( \rho \), perhaps indicating in this picture that not all triplet vibrations couple intramolecularly to the excited \( A_a \) levels, or that \( x^2 \) is a decreasing function of vibrational energy. The relative energy dependence of \( \rho \) is nearly identical over the range of excess vibrational energies considered here for all three glyoxal isotopes, and the magnitudes of \( \rho \) are quite similar \( (\rho_{(d)} / \rho_{(h)} \approx 2.0 \) and \( \rho_{(hd)} / \rho_{(h)} \approx 1.5 \) at all \( E_{\text{VIB}} \)). Only small differences in the coupling coefficients are required to produce the same magnitude and vibrational energy dependence of \( k_a \) for the three isotopes. The mixed state model of Freed would thus appear capable of qualitatively explaining the strong vibrational energy dependence and the isotopic insensitivity of the observed quenching rate constants. In some disagreement with this picture, values of \( k_a \) for the \( 8^1 \) level do not seem to be anomalously large, even though \( 8^1 \) may be more strongly intramolecularly coupled to the \( A_a \) state.\(^{36,37}\) Indeed spectroscopic evidence of intramolecular, singlet-triplet mixing has thus far been observed only for \( 8^1 \), or combination levels involving \( 8^1 \).

It has been assumed thus far that the \( 3A_a \) state is the only triplet state energetically accessible from the optically excited levels of \( 1A_a \) glyoxal. Theoretical considerations\(^{44,45}\) suggest the existence of other triplets near the \( 3A_a \) state. The SCF calculations (with optimized geometries) of Dykstra and Schaefer\(^{44}\) predict a II – II' excitation produces a \( 2B_a \) state, lying below the \( 3A_a \) state. Leclercq et al.\(^{46}\) employing CNDO/s techniques with configuration interaction, predict a \( 2B_a \) state to lie approximately 0.6 eV above the \( 3A_a \). Similar calculations on the analogous \( 3A_a \) and \( 3B_a \) states in biacyclo\(^{45,46}\) were in qualitative agreement with indirect (i.e., not a complete spectral analysis) experimental estimates\(^{45,46}\) of the positions of these states.

There have been no direct experimental observations of triplets other than the \( 3A_a \) in the case of glyoxal; however the large collisional quenching rates for high vibrational levels of \( 1A_a \) glyoxal\(^{25,28}\) could conceivably be
related to the opening of an additional channel for collisional ISC.

V. CONCLUSIONS

Collision-free lifetimes are reported for a number of vibronic levels of $^1A_\text{u}$ glyoxal−d$_2$ and $^1A^\text{e}$ glyoxal−hdf and are compared with previous results for $^1A_\text{u}$ glyoxal−h$_2$. While quantum yield data are required to obtain precise nonradiative rates, one can already say that the collision free loss rate of glyoxal−h$_2$ is primarily nonradiative, and that of glyoxal−d$_2$ is primarily radiative. The isotope effect on collision-free nonradiative decay is large, with $k_{\text{nuc}}(h_2)/k_{\text{nuc}}(d_2)>6$ for the vibrationless level of $^1A_\text{u}$ glyoxal. The nonradiative loss rates of glyoxal−h$_2$ and $^1A_\text{u}$ levels generally parallel the density of isoenergetic $^1A_\text{u}$ levels, but with a considerable dependence on specific vibrational levels. The dependences on specific vibrational levels are qualitatively in accord with the picture of Heller et al., which is based on the role of the optically excited mode as an accepting mode. We have no convincing explanation for the observation that in glyoxal−d$_2$ combinations of $\nu_8$ with increasingly energetic symmetric vibrations decay with increasingly long zero-pressure lifetimes, approaching that of the vibrationless $^1A_\text{u}$ state, but suggest that the reason is a decrease in the vibronically induced contribution to the radiative decay rate.

Rate constants for collisional depopulation of vibronic levels are also compared for the glyoxal isotopes. The rates for all three isotopes are strikingly similar when plotted as a function of vibrational energy in the $^1A_\text{u}$ ($^1A^\text{e}$) state. The rapid increase in $k_6$ with vibrational energy for high vibrational levels is apparently due to a corresponding increase in the intersystem crossing rate. The mixed state model of Freed seems capable of explaining qualitatively the energy dependence and isotope independence of the collisional quenching rate constants.

ACKNOWLEDGMENTS

We are pleased to acknowledge the assistance of P. Jones and useful discussions with Dr. R. A. Beyer and Professor K. Freed. This paper was prepared while one of us (WCL) enjoyed the hospitality and stimulating atmosphere of the Aspen Center for Physics.

*This work was supported by the National Science Foundation through grant number MPS75-01566.
†Present address: The Aerospace Corp., P. O. Box 92857, Los Angeles, CA 90009.
‡Camille and Henry Dreyfus Teacher–Scholar.

J. Chem. Phys., Vol. 66, No. 7, 1 April 1977