TIME AND ENERGY RESOLVED FLUORESCENCE OF *CIS*-GLYOXAL

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A pulsed, tunable dye laser has been used to excite the 0–0 band of *cis*-glyoxal near 4875 Å, at pressures from 30 to 150 mtorr. Fluorescence was resolved through a spectrometer and lifetines measured. Rate constants for the quenching of the vibrationless levels of the first excited singlet states of *cis*- and *trans*-glyoxal by argon, cyclohexane and glyoxal are presented. Quenching rates of *cis*-glyoxal are generally two to three times faster than the corresponding *trans* rates. A zero-pressure extrapolated lifetime of 0.96 ± 0.02 μsec is obtained for *cis*-glyoxal.

1. Introduction

Prior to 1970, glyoxal had been studied [1] in absorption and emission in the visible using conventional light sources, in microwave absorption, via electron diffraction, and in high resolution infrared studies [2]. The conclusion from this previous work is that only *trans*-glyoxal, a planar molecule of the C_{2h} point group, is observed.

Observation of the 4875 Å band system has been reported by Holzer and Ramsay [3]. Using the 4880 Å argon ion laser line for excitation, they identified the seven bands of this system shown in table 1. Currie and Ramsay [5] continued their work with a rotational analysis of a high resolution absorption study which led them to assign this system to the $^1B_1$–$^1A_1$ transition of *cis*-glyoxal. They also estimated that the lower level of the 4875 Å band system is 1125 ± 100 cm^{-1} above the *trans*-glyoxal ground state. Anderson [6] extended the work of Holzer and Ramsay and identified an additional band as belonging to this system. The microwave spectrum of *cis*-glyoxal has been investigated by Durig et al. [7].

Time-resolved fluorescence studies of *trans*-glyoxal have been reported by Yardley et al. [8] and Yardley [9]. By exciting the 0–0 band of *trans*-glyoxal near 4550 Å and viewing the fluorescence through filters which blocked scattered laser light, they were able to observe fluorescence from lower vibronic levels of the ^1A_u state.

2. Apparatus

The excitation source is a tunable dye laser [10] pumped by a 300 kW nitrogen laser [11]. The dye laser cavity consists of an antireflection coated cell containing the flowing dye, a diffraction grating (1800 lines/mm blazed at 5000 Å) and a dielectric coated output mirror (5% reflective at 4875 Å). With a mixture of 7-diethylamino-4-methylcoumarin and brilliant sulpha-

Table 1
The $^1B_1$–$^1A_1$ system of *cis*-glyoxal

λ_{air} (Å)	Assignment [a]
4875.3 [3]	0–0
5015.7 [3,6]	5_2^0 (ν_5: C–C–O bend)
5136.4 [3,6]	8_1^0 (ν_8: C–H wag)
5147.9 [6]	4_1^0 (ν_4: C–C stretch)
5212.6 [3,6]	$8_1^0 5_2^0$
5291.5 [3,6]	$8_1^0 5_2^0$
5329.1 [3,6]	2_1^0 (ν_2: C–O stretch)
5640.6 [3,6]	$8_1^0 2_1^0$

a) The identifications involving ν_5 differ from previous work and are taken from the more complete table of 14 bands of this system given by Dong and Ramsay [4].

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flavine in ethanol, the dye laser gives an output of about 10 kW peak power at 4875 Å in a pulse of less than 10 nsec duration with a spectral bandwidth of about 1.0 Å (fwhm). The addition of a 10-power telescope in the dye laser cavity reduces the spectral bandwidth by about an order of magnitude. Since for this experiment there was no noticeable difference in fluorescence between these two configurations, the wider exciting line was used. The repetition rate is typically 15 Hz.

The laser light is sent directly to an 8 cm diameter fluorescence cell which is connected to a standard glass vacuum system. Background pressures are typically 10^{-6} torr. Glyoxal pressure is measured with a capacitance manometer with rated accuracy of better than 1% over the range of 10 mtorr to 1 torr. The manometer head is held at a slightly elevated temperature to ensure stability and to reduce condensation in this region. A small pressure correction is made for thermal transpiration [12].

The fluorescence is observed perpendicular to the excitation through a 3/4 meter spectrometer with about 25 Å resolution for these data. At the lifetimes and pressures of this experiment, excited molecules do not diffuse from the field of view. The light through the spectrometer was detected by an RCA 1P28 photomultiplier. The amplified signal was digitized with 100 nsec resolution by a Biomation 610 transient recorder and summed in a PDP 8/E computer. At glyoxal pressures below 150 mtorr, the fluorescence from 6000 laser pulses was needed to obtain two decades of decay with *cis*-glyoxal. A least-squares fit is made to a single exponential since the data appear to have this behavior, as seen in fig. 1. Each resulting lifetime was corrected for the response time of the electronics ($\tau \approx 0.15$ μsec) and plotted as shown in figs. 2 and 3.

Glyoxal was prepared [13] by passing ethylene over a mixture of P_2O_5 and SeO_2 heated to about 200°C. It was purified by vacuum distillation and stored at dry ice temperature in a darkened, evacuated cell. There was no sign of loss of glyoxal in the fluorescence cell over the time of several consecutive runs of 6000 pulses. Leaving the cell filled up to 14 hours resulted in a few percent increase in measured lifetime, presumably due to a pressure drop from polymerization on the cell walls.

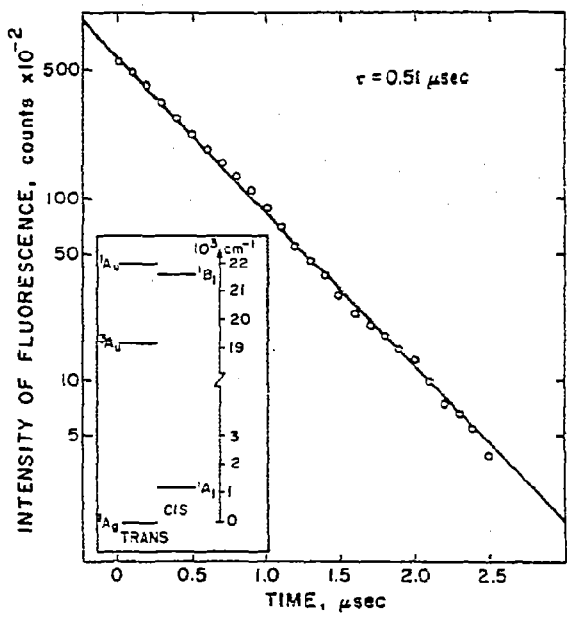

Fig. 1. Typical decay curve for the sum of 6000 pulses. The laser is exciting the *cis*-glyoxal 0–0 band. The fluorescence is primarily the 8_1^0 band at a pressure of about 127 mtorr of glyoxal. Inset is a diagram of the five levels observed for glyoxal.

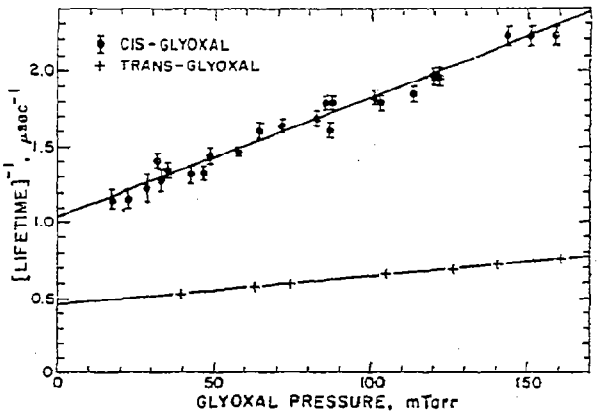

Fig. 2. (Lifetime)$^{-1}$ as a function of glyoxal pressure for *cis*- and *trans*-glyoxal fluorescence. In each case excitation is near the 0–0 band with the observed fluorescence being primarily the 8_1^0 band.

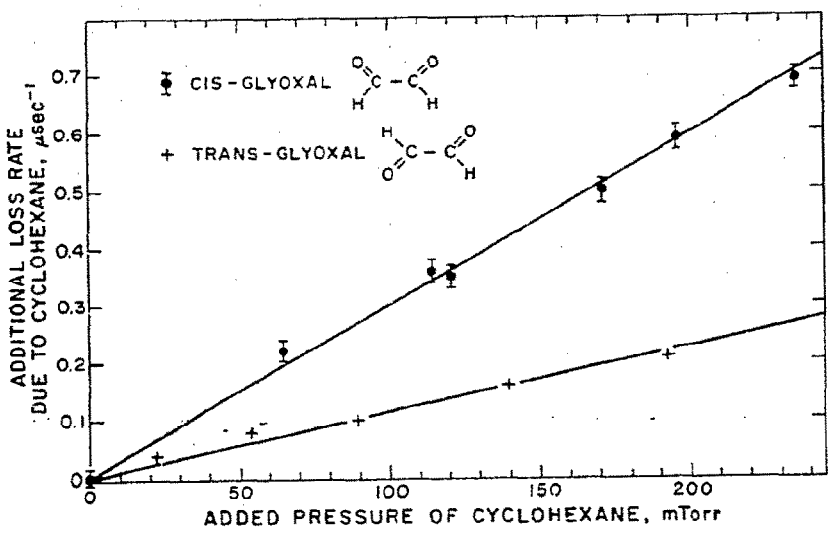

Fig. 3. Additional loss rate from the excited state as a function of cyclohexane added to a fixed glyoxal pressure of about 40 mtorr. For both *cis*- and *trans*-glyoxal, the 0–0 band is excited with the observed fluorescence being primarily the 8_1^0 band. The *cis* and *trans* ground state molecular geometries are shown.

3. Observations

Exciting glyoxal vapor at 4875 Å, identified [3,5] as the 0–0 band of *cis*-glyoxal, we observed emission bands with similar lifetime behavior centered near 4875, 5015, 5212, 5328 and 5142 Å. There is also the possibility of another band belonging to this system near 4817 Å. The first four of these are identified in table 1. Our strongest signal other than that at 4875 Å was obtained with the spectrometer centered at 5142 Å, probably the sum of the 8_1^0 band at 5136.4 Å and another band at 5147.9 Å, identified [6] as the 4_1^0. Tuning the laser 10 Å in either direction caused the fluorescence signal to disappear, indicating the absence of scattered light. The *cis*-glyoxal lifetime data shown in figs. 2 and 3 were taken exciting the 0–0 and observing the bands near 5142 Å. Data were also taken with the same excitation but with the spectrometer at 5212 and 5328 Å. In all of these cases the lifetimes at several pressures were the same within our experimental scatter. Thus our observations agree that each of these bands originates from the vibrationless $^1B_1$ level of *cis*-glyoxal.

As is clear from figs. 2 and 3, the quenching appears to obey simple Stern–Volmer kinetics [14]. The resulting rate constant for *trans*-glyoxal quenching of the vibrationless level of the first excited state of *cis*-glyoxal is $(1.40 \pm 0.05) \times 10^{-9}$ cm^3 sec^{-1} with a zero-pressure extrapolated lifetime of 0.96 ± 0.02 μsec. By fixing the glyoxal pressure at about 40 mtorr and adding a second gas, we measured the additional loss rate of the excited state as a function of increased pressure of the second gas, as shown in fig. 3. In this manner we measured the quenching rate constants for cyclohexane and argon. For comparison the 0–0 band of *trans*-glyoxal at 4550 Å was excited and the lifetime of its 8_1^0 band studied as a function of pressure for the same three gases. For the *trans*-glyoxal work, the fluorescence was resolved to about 2 Å. The results are summarized in tables 2 and 3.

We note that while exciting with 4875 Å light, one excites the *trans*-glyoxal hot band $8_1^0 5_1^0 7_1^1$. The 0–0 and 7_1^1 *trans*-glyoxal fluorescence bands have the same temporal characteristics as with excitation of the 7_1^1 band. Each of them also has about the same intensity as the strongest *cis*-glyoxal bands.

4. Discussion

The *trans*-glyoxal self-quenching rate constant in table 2 is consistent with that previously reported [8],

Table 2
Apparent quenching rate constants

Collision partner	*Trans*-glyoxal		*Cis*-glyoxal	
	rate constant (10^{-10} cm^3 sec^{-1})	number of collisions to quench a)	rate constant (10^{-10} cm^3 sec^{-1})	number of collisions to quench
trans-glyoxal	3.28 ± 0.05	4.2	14.0 ± 0.5	1.0
	3.50 ± 0.36 [8]	3.9		
cyclohexane	2.03 ± 0.07	9.9	5.34 ± 0.07	3.7
argon	1.02 ± 0.05	12.7	2.39 ± 0.09	5.4
	1.22 ± 0.18 [8]	10.6		

a) The collision frequency at 300°K is $2.56 \times 10^6 \times P \times \sigma_{AB}^2/\mu_{AB}^{1/2}$ where P is the pressure in torr, $\sigma_{AB} = \frac{1}{2}(\sigma_A + \sigma_B)$ is the mean molecular diameter in Å and μ_{AB} is the reduced mass of the collision partners in amu. Values used for σ are, 4.0, 6.1 and 3.4 Å for glyoxal, cyclohexane and argon, respectively.

Table 3
Extrapolated collision-free lifetimes (μsec)

Trans-glyoxal	*Cis*-glyoxal
2.17 ± 0.02	0.96 ± 0.02
2.16 ± 0.05 [8]	
2.24 [9]	

as is the zero-pressure extrapolated lifetime in table 3 [8,9]. However, with our apparatus we can resolve the fluorescence of *trans*-glyoxal to a few ångstroms or better. We observed [15] that when the 0–0 band of *trans*-glyoxal is excited, the torsional mode (ν_7) is populated from the vibrationless level via collisions. This effect is seen by observing the 7_1^1 fluorescence (about 20 Å away from the 0–0 band) which shows a relatively slow rise and subsequent decay with apparent pressure dependence for both the rise and decay rates. The rate of population of the torsional model from the vibrationless level in the ^1A_u excited state is significant even at 20 mtorr; at 200 mtorr it is approaching the response limit of the electronics. The low resolution *trans*-glyoxal data reported here are averages from at least two levels of the ^1A_u excited state. The solution of the kinetics involved in this vibrational transfer gives results for quenching rate constants and zero-pressure lifetime slightly different [15] from those of tables 2 and 3. In order to facilitate comparisons with earlier results and with our *cis*-glyoxal data, these corrections are not included here.

As noted by Currie and Ramsay [5], the absorption of the 0–0 band of *cis*-glyoxal is about three orders of magnitude less than that of the *trans*-glyoxal 0–0 band. Since the fluorescence signal level of *cis*-glyoxal is correspondingly lower, we found it necessary to increase the spectrometer aperture to the point that we were unable to resolve the fluorescence sufficiently to observe a similar vibrational effect in the $^1B_1$ state. Since this rapid collisional population of low energy modes is probably universal, it is most likely present in *cis*-glyoxal also.

From the integrated absorption spectrum of *trans*-glyoxal, it has been estimated [6] that the zero-pressure radiative lifetime should be about 10 μsec. It is clear from the observed lifetime that the losses from the ^1A_u state are dominated by non-radiative processes. Since the absorption of *cis*-glyoxal from its ground state is about the same as from equally populated *trans*-glyoxal states, it is likely that the lifetime of the $^1B_1$ state is also controlled by radiationless processes. The zero-pressure lifetimes are probably not seriously affected by any vibrational transfer effects since reasonably low pressure measurements have been made. Thus one can conclude that intramolecular radiationless losses of the vibrationless level of the $^1B_1$ state of *cis*-glyoxal are greater than the corresponding losses of the ^1A_u state of *trans*-glyoxal.

One possible non-radiative mechanism for loss of *cis*-glyoxal in the $^1B_1$ excited state is collisional conversion to the ^1A_u excited state of *trans*-glyoxal. However, when exciting at 4875 Å, we observed that the

0–0 and 7_1^1 bands of *trans*-glyoxal have the same temporal characteristics as if direct excitation of the 7^1 level had taken place. Also, no *trans*-glyoxal band originating from any other level was observed, so *cis–trans* conversion is probably not important from low levels of the $^1B_1$ state. A second loss mechanism is internal conversion to either of the unobserved ^1B_g or $^1A_2$ states or to high vibrational levels of the ^1A_g and $^1A_1$ ground states of *trans*- and *cis*-glyoxal. The third possibility is for intersystem crossing to the ^3A_u or ^3B_g states of *trans*-glyoxal or to the $^3B_1$ or $^3A_2$ states of *cis*-glyoxal. The $^3B_1$ state has not yet been identified; no studies have been made to correlate loss of the $^1B_1$ state with gain of the $^3B_1$ or ^3A_u states.

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