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Laser induced fluorescence and phosphorescence of matrix isolated glyoxal: Evidence for exciplex formation in the $\tilde{A}^1A_u$ and $\tilde{a}^3A_u$ states

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Laser-induced fluorescence ($\tilde{A}^1A_u \rightarrow \tilde{X}^1A_g$) and phosphorescence ($\tilde{a}^3A_u \rightarrow \tilde{X}^1A_g$) as well as absorption and excitation spectra of glyoxal in Ar, N₂, and CO matrices have been measured at 12 K. Supplementary infrared absorption spectra have also been taken. Although the dominant band in the absorption and excitation spectra is the 0₀⁰ transition, it is absent in both the fluorescence and phosphorescence spectra leading to the hypothesis that glyoxal forms an exciplex with its nearest neighbor(s) in both the $\tilde{A}^1A_u$ and $\tilde{a}^3A_u$ states. The equilibrium configuration of the nuclei is distorted in the exciplex producing, after fluorescence or phosphorescence, ground state glyoxal molecules born vibrationally excited while the Franck-Condon factors for the 0₀⁰ transition vanish. In argon the fundamentals ν_7 and ν_{12} are preferentially excited, corresponding to two different isomers of the complex, while in N₂ and CO an unambiguous assignment for the preferentially excited modes cannot be given. The rule of mutual exclusion still holds in the IR spectra, in agreement with the formation of an excited rather than a ground state complex. Fluorescence and phosphorescence lifetimes place limits on the quantum yields of the various deexcitation channels and show that localized phonon modes play a dominant role in coupling to the matrix.

I. INTRODUCTION

The low-lying excited electronic states of gas phase glyoxal have been studied spectroscopically since the early part of this century.^{1,2} On the basis of the vibrational analysis of the visible absorption spectrum, Brand³ pointed out that the transition to the first excited electronic state was of the type $^1A_u \leftarrow ^1A_g$. This transition involves the excitation of a nonbonding electron largely localized on one of the carbonyl oxygen atoms, to the antibonding π^* orbital of that group.⁴ The existence of the corresponding triplet state (3A_u), with the same electronic configuration as the 1A_u state, was demonstrated using magnetic rotation spectroscopy.⁵ Extensive high resolution spectroscopic studies by Ramsay and co-workers revealed the precise geometry of the molecule from rotational analysis⁶ and showed, using laser-induced fluorescence techniques, that the *cis* isomer is present to a minor extent as well.⁷

Since glyoxal is intermediate in size, between the small and large molecular limits, it presents a unique opportunity for the study of intramolecular energy transfer dynamics. Avouris *et al.*⁸ reviewed much of the work prior to 1977 in which lifetimes and various luminescence yields were measured as a function of pressure,⁹⁻¹¹ excitation energy,^{12,13} and collision partners.¹⁴⁻¹⁷ The nonradiative decay from S_1 to S_0 in glyoxal was found to behave in the large molecule

(statistical) limit while coupling between S_1 and T_1 could be described in terms of the weak coupling limit of the small molecule case in which only collision-induced intersystem crossing occurs. Recently, experiments in supersonic beams showed the existence of Ar-glyoxal complexes by fluorescence excitation spectra.¹⁸ Further investigations on the vibrational predissociation of these complexes¹⁹ showed the existence of two different isomeric forms. In addition, the vibronic 7₁⁰ transition, forbidden in free gas phase glyoxal, was measured in fluorescence spectra of the complex suggesting a strong coupling of the torsional vibration (ν_7) with the van der Waals modes.

Thompson² measured the first infrared spectrum of gas phase glyoxal while a reliable vibrational analysis was given by Harris.²⁰ Rotational analysis of the high resolution infrared spectrum²¹ further refined the vibrational frequencies. Planarity of the molecule is preserved upon condensation as shown by the infrared spectra of polycrystalline glyoxal and of glyoxal isolated in a nitrogen matrix.²²

A previous study of matrix isolated glyoxal,²³ mainly devoted to the investigation of matrix photochemistry, reported laser-induced emission spectra. Although those experiments showed predominantly emission from the $\tilde{a}^3A_u$ state, implying that intersystem crossing was enhanced in the matrix, complex formation was not considered in interpreting the spectrum.

In this study, laser-induced fluorescence and phosphorescence as well as infrared and visible absorption spectra of

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FIG. 1. Schematic of the experimental setup used for measuring laser excited emission. BE represents the beam expander, D the diaphragm, C the cryostat, A the aluminum substrate, L the focusing lenses, P the dove prism, and PMT the photomultiplier tube.

glyoxal in Ar, N₂, and CO matrices are presented and analyzed. Glyoxal in its first excited electronic state is shown to form an exciplex with its nearest neighbor(s) in all three matrices, and transitions normally forbidden dominate the emission spectra. The spectral characteristics of these complexes are similar to those of the Ar-glyoxal complex found in supersonic beam experiments. Due to the matrix cage effect, no vibrational predissociation is observed. In addition, the phosphorescence lifetime has been determined and an upper limit is given for the fluorescence lifetime. This, in combination with the relative intensities of fluorescence and phosphorescence can be used to place limits on the quantum yields of the various relaxation processes.

The main motivation for carrying out this spectroscopic study originates in the need to understand the spectroscopic properties of glyoxal embedded in astrophysically relevant molecular mixtures ("dirty ices"). This interest arises from the fact that glyoxal is readily formed by the recombination of HCO radicals isolated in the molecular mixtures, and that HCO is a likely constituent of interstellar ices.²⁴ These ices, comprised primarily of molecules such as H₂O, CO, CH₄, and NH₃, coat interstellar dust particles and are presumed to make up the icy components of comets in the solar system.^{25,26} Consequently, emission from glyoxal can be used to probe the recombination of HCO radicals in the laboratory, yielding further insight into the dynamics of diffusion controlled processes in low temperature solids as well as information concerning an important astrophysical process.

II. EXPERIMENTAL

Monomeric glyoxal vapor was prepared by heating the trimer hydrate (Merck, analysis quality) covered with P₂O₅ under vacuum at 180–200 °C. It was then collected at dry ice temperature, purified by several distillation cycles and finally stored at 77 K. Gas mixtures of the matrix material and glyoxal, usually in the ratio 500/1 (MR = 500), were prepared by using standard manometric techniques on a greaseless vacuum line. The gases: Ar U.H.P. 99.999% (Matheson); N₂ 99.995% (Hoek Loos); CO 99.997% (Hoek Loos)

were used without further purification. The gaseous mixtures were generally deposited for 30 min at a rate of ~3 mmol/h onto a 12 K aluminum substrate cooled by an Air Products CSA-202 displacer closed cycle refrigeration system.

A schematic of the experimental setup used for measuring emission and excitation spectra is shown in Fig. 1. Optical excitation is provided by a combination of a XeCl excimer laser (Lambda Physik EMG 100) and a dye laser (Lambda Physik FL 2000) operated with either Coumarin 120 (lasing from 423 to 462 nm) or Coumarin 2 (431–475 nm). The laser system was typically run at a repetition rate of 1.5 Hz and provided ~3 mJ pulses each with a duration of ~15 ns. Before entering the cryostat the beam passed through an expander and a diaphragm to lower the beam intensity enough to prevent sample warmup and destruction. The collection optics consists of two lenses designed to match the *f* number of the Spex double monochromator (model 1672, focal length 2×0.25 m) and a dove prism to rotate the image into coincidence with the entrance slit. The resolution employed in the fluorescence spectra was 0.3 nm while 0.6 nm was used with the phosphorescence spectra. Emission signals were detected with a low noise photomultiplier (ITT-FW 130) in combination with a transient digitizer (Gould Biomation model 4500). For all spectra shown, the vertical axis is linear. Occasionally an Ortec amplifier (model 9302) was used to measure fluorescence lifetimes in the nanosecond domain before entering the digitizer. The trace of emission signal decay was typically averaged over 64 laser shots and subsequently dumped into the memory of a

FIG. 2. The $\tilde{A}^1A_u \leftarrow \tilde{X}^1A_g$ transition of glyoxal isolated in Ar, N₂ and CO matrices at 12 K (MR = 500). See Table I for band positions and assignments. Calibration lines of a low pressure Hg lamp are at 405.7 and 435.8 nm. These spectra are not corrected for spectral sensitivity.

TABLE I. Vibronic absorption bands and assignments for the $\tilde{A}^1A_u \leftarrow \tilde{X}^1A_g$ transition of glyoxal isolated in several matrices (MR = 500).

Transition	Ar (site II) (nm)	Ar (site I) (nm)	Gas ^a (nm)	N ₂ (nm)	CO (nm)
0 ₀ ⁰	462.0	459.7	455.0	451.5	450.8
5 ₀ ¹	451.1	449.2	444.7		
8 ₀ ⁰	+ ^b	444.2	440.3	437.9 ^c	438.5 ^c
4 ₀ ¹		440.1	436.1		
8 ₀ ¹ 5 ₀ ¹		+ ^b	430.6	424.3 ^c	424.0 ^c
2 ₀ ¹		431.8	427.9		

^aReference 3 except for 4₀¹ taken from Ref. 13.

^bVery weak absorption band present.

^cIn N₂ and CO matrices an unambiguous assignment is not possible.

homemade microcomputer. Tuning of the dye laser and monochromator frequencies with the triggering of the excimer laser, and stepping of the stripchart recorder as well as further data handling were also carried out by this microcomputer.

Visible absorption spectra, with a resolution of 0.6 nm, were measured in reflection by replacing the PMT in Fig. 1 by a 250 W quartz-halogen lamp and installing a Hamamatsu R 928 UH photomultiplier (S-20) at the laser beam entrance window of the cryostat.

Infrared absorption spectra were measured from 4000–400 cm⁻¹ with a resolution of 1 cm⁻¹ using a Digilab (FTS-15 BD) Fourier transform infrared spectrometer with equipment previously described.²⁷

III. RESULTS

A. Visible absorption spectra

The visible absorption spectra of glyoxal in Ar, N₂, and CO matrices (MR = 500) are shown in Fig. 2. The measured absorption frequencies are listed in Table I together with the observed gas phase values of the $\tilde{A}^1A_u \leftarrow \tilde{X}^1A_g$ transition. The assignments in argon are based on the close proximity with the gas phase spectrum and are in agreement with those given by Diem *et al.*²³ While the spectrum in argon is red shifted with respect to that in the gas phase and shows evidence for two sites, the spectra in N₂ and CO matrices are blue shifted and contain no resolvable structure. Although the width of the bands in N₂ and CO prevents making an unambiguous assignment, the 0₀⁰ transition can be reliably identified by its intensity and position.

B. Excitation spectra

Two different types of excitation spectra have been recorded, i.e., fluorescence excitation spectra with the monochromator tuned to one of the main fluorescence bands (usually 492.0 nm for site I and 488.4 nm for site II in argon) and phosphorescence excitation spectra with the monochromator tuned to the strongest phosphorescence emission peak (usually 537.0 nm for site I and 533.0 nm for site II in argon). Since the structure of both types is similar and closely

resembles that of the absorption spectra presented in the previous section they will not be treated separately.

In argon, two different sites have been observed as shown in Fig. 3. The excitation spectra from both sites are red shifted with respect to the gas phase spectrum, with that from site I 90 ± 10 cm⁻¹ to the blue of that from site II. Site I clearly exhibits sharp zero phonon lines while site II shows broader, less structured features. The features which originate from site II have only weak to moderate counterparts in absorption as shown in Fig. 2. The wavelengths of the zero phonon lines for site I and of the intensity maxima of all the other bands have been listed in Table II together with their assignments. No differences in the excitation spectra were measured as MR was varied from 50 to 5000.

Figure 4 shows the excitation spectra for glyoxal in N₂ and CO matrices (MR = 500). Both spectra are blue shifted with respect to the gas phase spectrum and characterized by broad bands which resemble their absorption counterpart. Wavelengths of maximum intensity and assignments are listed in Table II.

FIG. 3. The phosphorescence ($\tilde{a}^3A_u \rightarrow \tilde{X}^1A_g$) and fluorescence ($\tilde{A}^1A_u \rightarrow \tilde{X}^1A_g$) excitation spectrum from glyoxal isolated in sites I and II in an argon matrix at 12 K (MR = 500). See Table II for band positions and assignments. The detection wavelength is indicated by λ_d . These spectra are not corrected for spectral sensitivity. The dye laser was operated with Coumarin 2.

TABLE II. Band positions (in nm) and assignments of the phosphorescence excitation spectra for the $\tilde{A}^1A_u \leftarrow \tilde{X}^1A_g$ transition of glyoxal isolated in several matrices (MR = 500).

Transition	Ar (site II) [$\lambda_d = 533.0$] ^b	Ar (site I) [$\lambda_d = 537.0$] ^b	Gas ^a	N ₂ [$\lambda_d = 536.0$] ^b	CO [$\lambda_d = 543.0$] ^b
0 ₀ ⁰	461.6	459.9	455.2	452.0	451.0
5 ₀ ¹	451.2	449.7	444.7	439.0	439.4
8 ₀ ¹	446.8	444.8	440.3		
4 ₀ ¹	442.6	440.7	436.0		
8 ₀ ¹ 5 ₀ ¹	437.2	435.4			
2 ₀ ¹	434.0	432.1	427.9		

^aReference 13.^bDetection wavelength in nm.

C. Fluorescence and phosphorescence spectra

Fluorescence and phosphorescence spectra were systematically recorded with excitation into each individual vibrational level of the $\tilde{A}^1A_u$ state which appeared in the absorption or excitation spectra. For reference throughout the following the fundamental vibrational frequencies of gas phase glyoxal in the $\tilde{a}^3A_u$, $\tilde{A}^1A_u$, and $\tilde{X}^1A_g$ states have been compiled from the literature and listed in Table III.

FIG. 4. Phosphorescence ($\tilde{a}^3A_u \rightarrow \tilde{X}^1A_g$) excitation spectra from glyoxal isolated in N₂ and CO matrices at 12 K (MR = 500). See Table II for band positions and assignments. The detection wavelength is indicated by λ_d . These spectra are not corrected for spectral sensitivity. Coumarin 102 was used in the dye laser.

In argon two different fluorescence spectra corresponding to emission from either site I or site II have been observed. The spectra are independent of concentration (MR varying between 50 and 5000). Both have similar structure and are shown in Fig. 5. Wavelengths of maximum intensity, assignments, relative intensities, and vibrational spacings with respect to the 0₀⁰ transition of glyoxal in the matrix (ΔE_m) are listed in Table IV. For comparison, vibrational spacings of the same transition in the gas phase are also listed in Table IV (ΔE_{gas}).

Surprisingly, the fluorescence spectrum observed after excitation into site I is $147 \pm 15 \text{ cm}^{-1}$ red shifted with respect to the fluorescence spectrum observed after excitation into site II. Thus, the shifts in the excitation and fluorescence spectra are opposite in direction. Fluorescence spectra from both sites do not show zero phonon lines and, furthermore, their structure does not change with excitation into the different absorption bands corresponding to each site, indicating fast vibrational relaxation in the $\tilde{A}^1A_u$ state. Another remarkable aspect of these spectra is the absence of any emission at the 0₀⁰ position for the transition to the $\tilde{A}^1A_u$ state, the strongest band in the absorption and excitation spectra.

Similar behavior was found for the phosphorescence spectra in argon (MR = 50–5000). Again, as shown in Fig.

TABLE III. Fundamental vibrational frequencies (in cm⁻¹) of gas phase glyoxal in various electronic states.^a

Symmetry	Vibration	$\tilde{X}^1A_g$	$\tilde{A}^1A_u$	$\tilde{a}^3A_u$
a_g	ν_1 C–H stretch	2843	2809	
	ν_2 C = O stretch	1745	1391	1458
	ν_3 C–H rock	1338		
	ν_4 C–C stretch	1065	955	963
	ν_5 C–C = O bend	550	509	502
a_u	ν_6 C–H wag	801	718 ^b	
	ν_7 torsional	127	233	234
b_g	ν_8 C–H wag	1048	735	
b_u	ν_9 C–H stretch	2835		
	ν_{10} C = O stretch	1732		
	ν_{11} C–H rock	1312		
	ν_{12} C–C = O bend	339	380	391

^aReference 31 and references therein.^bReference 17.

FIG. 5. Fluorescence ($\tilde{A}^1A_u \rightarrow \tilde{X}^1A_g$) and phosphorescence ($\tilde{a}^3A_u \rightarrow \tilde{X}^1A_g$) spectra from glyoxal isolated in an argon matrix at 12 K (MR = 500). See Tables IV and V for band positions and assignments. The excitation wavelength was 444.8 nm for site I and 446.8 for site II. These spectra are not corrected for spectral sensitivity.

5, two different spectra were observed corresponding to emission from site I and site II. Wavelengths of maximum intensity, assignments, and relative intensities are listed in Table V together with line positions calculated as explained in Sec. IV. The spectrum observed upon excitation in site I was $141 \pm 15 \text{ cm}^{-1}$ red shifted with respect to that found

upon excitation in site II. Again, no change in the spectrum was found with excitation in the different absorption bands corresponding to each site. As with fluorescence, no zero phonon lines were seen.

Excitation in one of the two sites always produces some emission from the other site as shown in Fig. 5. This implies

TABLE IV. Glyoxal fluorescence ($\tilde{A}^1A_u \rightarrow \tilde{X}^1A_g$) band positions, relative intensities, and identifications from sites I and II in an argon matrix at 12 K (MR = 500). ΔE_{gas} is the spacing between each transition and the 0_0^0 energy in the gas while ΔE_m is the corresponding spacing measured in the matrix.

Argon site I				Argon site II			
Transition	λ_m^a (rel. I) ^c (nm)	$\Delta E_m^{b,c}$ (cm^{-1})	ΔE_{gas}^d (cm^{-1})	Transition	λ_m^a (rel. I) ^c (nm)	$\Delta E_m^{b,c}$ (cm^{-1})	ΔE_{gas}^d (cm^{-1})
12_0^0	468.0 (1)	371	339	7_1^0	464.6 (1)	130	127
$12_0^0 7_2^0$	474.6 (0.03)	669	593				
$12_1^0 5_1^0$	480.2 (0.06)	914	889	$7_1^0 5_1^0$	476.6 (0.07)	672	677
$12_1^0 5_1^0 7_2^0$	486.0 (<0.01)	1163	1127				
$12_1^0 8_1^0$	492.2 (0.5) ^f	1422	1387	$7_1^0 8_1^0$	488.4 (0.7) ^f	1179	1175
$12_1^0 4_1^0$			1404	$7_1^0 4_1^0$			1192
$12_1^0 5_2^0$			1439	$7_1^0 5_2^0$			1227
$12_1^0 8_1^0 5_1^0$			1937	$7_1^0 8_1^0 5_1^0$			1725
$12_1^0 4_1^0 5_1^0$	505.2 (0.04) ^f	1945	1954	$7_1^0 4_1^0 5_1^0$	502.0 (0.07) ^f	1734	1742
$12_1^0 2_1^0$	508.4 (0.05)	2069	2084	$7_1^0 2_1^0$	505.0 (0.06)	1852	1872
$12_1^0 8_2^0$	518.8 (0.05) ^f	2464	2435	$7_1^0 8_2^0$	514.8 (0.04) ^f	2229	2223
$12_1^0 8_1^0 4_1^0$			2452	$7_1^0 8_1^0 4_1^0$			2240
$12_1^0 4_2^0$			2469	$7_1^0 4_2^0$			2257

^a Wavelength uncertainty $\pm 0.2 \text{ nm}$.

^b Uncertainty in frequencies $\pm 25 \text{ cm}^{-1}$.

^c Assuming $0_0^0 = 460.0 \text{ nm}$, for site I and $0_0^0 = 461.8 \text{ nm}$ for site II.

^d The vibrational frequencies are taken from Table III.

^e These instrument-corrected intensities are scaled relatively only within each spectrum.

^f An unambiguous assignment cannot be made.

TABLE V. Glyoxal phosphorescence ($\tilde{a}^3A_u \rightarrow \tilde{X}^1A_g$) band positions, relative intensities, and identifications from sites I and II in an argon matrix at 12 K (MR = 500). See Sec. IV C for a description of the wavelength calculation.

Argon site I			Argon site II		
Transition	λ_m^a (rel. I) ^b (nm)	λ_{calc}^c (nm)	Transition	λ_m^a (rel. I) ^b (nm)	λ_{calc}^c (nm)
12_1^0	537.0 (1)	537.1	7_1^0	533.0 (1)	532.9
$12_1^0 7_2^0$	545.5 (0.02)	543.9			
$12_1^0 5_1^0$	553.5 (0.02)	553.4	$7_1^0 5_1^0$	548.5 (0.009)	549.0
$12_1^0 8_1^0$	569.5 (0.13) ^d	569.1	$7_1^0 8_1^0$	564.5 (0.01) ^d	564.4
$12_1^0 4_1^0$		569.6	$7_1^0 4_1^0$		564.9
$12_1^0 5_2^0$		570.8	$7_1^0 5_2^0$		566.1
$12_1^0 3_1^0$		578.7	$7_1^0 3_1^0$	573.5 (0.0003)	573.8
	582.0 (0.0002)			577.0 (<0.0001)	
$12_1^0 2_1^0$	592.0 (0.05)	592.6	$7_1^0 2_1^0$	587.0 (0.08)	587.5
$12_1^0 8_2^0$	605.5 (0.02) ^d	605.2	$7_1^0 8_2^0$	600.5 (0.01) ^d	599.9
$12_1^0 8_1^0 4_1^0$		605.8	$7_1^0 8_1^0 4_1^0$		600.5
$12_1^0 4_2^0$		606.4	$7_1^0 4_2^0$		601.1
$12_1^0 8_1^0 2_1^0$		616.0			
$12_1^0 8_1^0 2_1^0$	631.0 (0.008) ^d	631.8	$7_1^0 8_1^0 2_1^0$	626.5 (0.008) ^d	626.1
$12_1^0 4_1^0 2_1^0$	632.5	632.5	$7_1^0 4_1^0 2_1^0$		626.8
$12_1^0 8_3^0$		646.1	$7_1^0 8_3^0$		640.2
$12_1^0 8_2^0 4_1^0$	646.0 (0.0008) ^d	646.9	$7_1^0 8_2^0 4_1^0$	640.0 (0.002) ^d	640.9
$12_1^0 8_1^0 4_2^0$		647.6	$7_1^0 8_1^0 4_2^0$		641.6

^a Wavelength uncertainty ± 0.7 nm.

^b These instrument-corrected intensities are scaled relatively only within each spectrum.

^c Assuming $0_0^0 = 527.2$ for site I and $0_0^0 = 529.6$ for site II and $\nu_{12} = 349 \text{ cm}^{-1}$ and $\nu_7 = 116 \text{ cm}^{-1}$.

^d An unambiguous assignment cannot be made.

FIG. 6. Fluorescence ($\tilde{A}^1A_u \rightarrow \tilde{X}^1A_g$) and phosphorescence ($\tilde{a}^3A_u \rightarrow \tilde{X}^1A_g$) spectra from glyoxal in N_2 and CO matrices at 12 K (MR = 500). See Tables VI and VII for band positions and assignments. The excitation wavelength was 440 nm in both matrices. These spectra are not corrected for spectral sensitivity.

TABLE VI. Glyoxal fluorescence ($\tilde{A}^1A_u \rightarrow \tilde{X}^1A_g$) band positions, relative intensities, and identifications in N_2 and CO matrices 12 K ($MR = 500$). ΔE_{gas} is the spacing between each transition and the 0_0^0 level while ΔE_m is the corresponding spacing measured in the matrix.

N_2 matrix				CO matrix			
Transition	λ_m^c (rel. I) ^d (nm)	ΔE_m (cm^{-1})	ΔE_{gas}^e (cm^{-1})	Transition ^b	λ_m^c (rel. I) ^d (nm)	ΔE_m (cm^{-1})	ΔE_{gas}^f (cm^{-1})
x_y^0	466.5 (1)	688 ± 50	678	x_y^0	473.5 (1)	1066 ± 70	1048
$x_y^0 5_1^0$	477.5 (0.08)	1182 ± 70	1228				
$x_y^0 8_1^0$	491.0 (0.4) ^g	1758 ± 50	1726	$x_y^0 8_1^0$	497.5 (0.3) ^g	2072 ± 70	2096
$x_y^0 4_1^0$			1743	$x_y^0 4_1^0$			2113
$x_y^0 5_2^0$			1778	$x_y^0 5_2^0$			2148
$x_y^0 4_1^0 5_1^0$			2276	$x_y^0 8_1^0 5_1^0$			2646
$x_y^0 4_1^0 5_1^0$	505.5 (0.1) ^g	2342 ± 70	2293	$x_y^0 4_1^0 5_1^0$	511.5 (0.07) ^g	2623 ± 70	2663
$x_y^0 8_2^0$			2774	$x_y^0 8_2^0$			3144
$x_y^0 8_1^0 4_1^0$	518.0 (0.06) ^g	2819 ± 70	2791	$x_y^0 8_1^0 4_1^0$	526.0 (0.02) ^g	3162 ± 70	3161
$x_y^0 4_2^0$			2808	$x_y^0 4_2^0$			3178

^a Assuming $0_0^0 = 452.0$ nm in a N_2 matrix and the gas phase vibrational frequencies for ν_4 , ν_5 , and ν_8 the average value of x_y^0 is found to be $698 \pm 35 \text{ cm}^{-1}$.

^b Assuming $0_0^0 = 451.0$ nm, in a CO matrix and the gas phase vibrational frequencies for ν_4 , ν_5 , and ν_8 the average value of x_y^0 is found to be $1028 \pm 35 \text{ cm}^{-1}$.

^c Wavelength uncertainty ± 1 nm.

^d These instrument-corrected intensities are scaled relatively only within each spectrum.

^e Calculated spacings with $x_y^0 = 12_2^0$. If $x_y^0 = 7_1^0 5_1^0$ all spacings have to be lowered 1 cm^{-1} .

^f Calculated spacings with $x_y^0 = 8_1^0$. If $x_y^0 = 4_1^0$ all spacings have to be lowered 18 cm^{-1} .

^g An unambiguous assignment cannot be made.

that either excitation into the tail of the absorption band of the second site or energy transfer between the sites is responsible. The lack of dependence of the emission spectra on concentration suggests that the former mechanism holds.

Fluorescence and phosphorescence spectra also have been recorded in N_2 and CO matrices ($MR = 50\text{--}5000$) as shown in Fig. 6. Analogous to the excitation and absorption spectra in N_2 and CO, the bands are broadened and, furthermore, no indications of different sites have been found. The wavelengths of maximum intensity and the assignments for the fluorescence spectra in both matrices are listed in Table VI together with the vibrational spacings with respect to the 0_0^0 in transition in the pertinent matrix (ΔE_m) and the corresponding gas phase spacings (ΔE_{gas}). Again, surprisingly, no emission from the position of the electronic origin has

been observed in N_2 or in CO. For the phosphorescence spectra, wavelengths of maximum intensity, assignments, relative intensities, and expected line positions (see Sec. IV) are listed in Table VII. Finally, the phosphorescence as well as fluorescence spectra did not change with excitation into the various absorption bands in N_2 or CO.

In addition to recording emission spectra, fluorescence and phosphorescence lifetimes of individual vibronic transitions have been measured as well. These are listed in Table VIII. In Ar, N_2 , and CO matrices the lifetimes are independent of excitation energy and, within one spectrum (fluorescence or phosphorescence), the lifetimes measured for each vibronic transition were equal to within the error bars. The uncertainties in the lifetimes listed in Table VIII, which are larger than the errors in an individual experiment, owe their origin to variations between different experiments.

Another set of experiments has been carried out using the excimer laser ($\lambda = 308.0$ nm) as excitation source to

TABLE VII. Glyoxal phosphorescence ($\tilde{a}^3A_u \rightarrow \tilde{X}^1A_g$) band positions, relative intensities, and identifications in N_2 and CO matrices at 12 K ($MR = 500$). Calculated wavelengths were derived as explained in Sec. IV.

N_2 matrix			CO matrix		
Transition	λ_m^a (rel. I) ^b (nm)	λ_{calc}^c (nm)	Transition	λ_m^a (rel. I) ^b (nm)	λ_{calc}^d (nm)
x_y^0	536.0 (1)	536.1	x_y^0	543.0 (1)	544.4
$x_y^0 8_1^0$	567.0 (0.1) ^e	568.0	$x_y^0 8_1^0$	574.5 (0.09) ^e	577.3
$x_y^0 4_1^0$		568.6	$x_y^0 4_1^0$		577.8
$x_y^0 5_2^0$		569.7	$x_y^0 5_2^0$		579.0
$x_y^0 2_1^0$		591.5	$x_y^0 2_2^0$		601.4
$x_y^0 2_1^0$	589.5 (0.07)	591.5		597.5 (0.06)	

^a Wavelength uncertainty 2 nm.

^b These instrument-corrected intensities are scaled relatively only within each progression.

^c Assuming $0_0^0 = 516.8$ nm and $x_y^0 = 698 \text{ cm}^{-1}$ in a N_2 matrix.

^d Assuming $0_0^0 = 516.8$ nm and $x_y^0 = 1028 \text{ cm}^{-1}$ in a CO matrix.

^e An unambiguous assignment cannot be made.

TABLE VIII. Fluorescence (f) and phosphorescence (p), lifetimes (τ), intensity ratios (I_p/I_f), and quantum efficiencies (ϕ) for glyoxal in Ar, N_2 , and CO matrices. Intersystem crossing and internal conversion are abbreviated as isc and ic, respectively.

	Gas	Ar (site I)	Ar (site II)	N_2	CO
τ_f (μs)	4.1 ^a	<0.045	<0.045	<0.045	<0.045
τ_p (ms)	3.29 ^b	2.1 ± 0.1	2.2 ± 0.1	1.7 ± 0.1	1.3 ± 0.1
I_p/I_f		12.5 ± 1	13.5 ± 1	34 ± 1	4.7 ± 0.1
ϕ_f	0.58 ^a	<0.02	<0.02	<0.02	<0.02
ϕ_p		~ 0.93	~ 0.97	~ 0.77	~ 0.58
ϕ_{isc}		<0.27	<0.28	<0.88	<0.16
ϕ_{ic}		>0.71	>0.70	>0.10	>0.82

^a Reference 30.

^b Reference 16.

FIG. 7. Infrared absorption spectra in the regions of the fundamental vibrations of glyoxal isolated in Ar, N₂, and CO matrices at 12 K (MR = 500 and 50). See Table IX for band positions and assignments. The relative intensities of the different modes cannot be determined from this figure because different absorbance scales have been used to normalize the peaks.

excite glyoxal in its second excited singlet state (1B_g). While the spectral structure of the fluorescence and phosphorescence spectra remained unchanged with respect to that presented above, the relative intensity of fluorescence to phosphorescence increased. In argon, emission from both sites was observed simultaneously, with that from site I slightly more intense than that from site II. During each of these experiments the intensity of glyoxal emission decreased as a function of exposure time. This is presumably due to the photolysis of glyoxal to formaldehyde and carbon monoxide²³ as shown by the corresponding growth of fluorescence from the $\tilde{A} \ ^1A_2 \rightarrow \tilde{X} \ ^1A_1$ transition of formaldehyde.²⁸

D. Infrared spectra

In addition to the visible absorption and emission spectra, infrared absorption spectra from 4000 to 500 cm⁻¹ of glyoxal in Ar, N₂ and CO matrices (MR = 500 and 50) have also been measured. The IR active fundamentals: ν_6 (CH wag), ν_9 (CH stretch), ν_{10} (CO stretch), and ν_{11} (CH rock) have been observed in all three matrices with the salient regions of the spectra shown in Fig. 7. A complete list of all

measured infrared absorptions due to glyoxal and their assignments are listed in Table IX together with their gas phase counterparts.

IV. DISCUSSION

A. Infrared spectra

Comparison of the IR active fundamentals of matrix isolated glyoxal with gas phase data²⁰ (Table IX) allows us to draw some conclusions about matrix interactions.

All IR active fundamentals involving the CH bond i.e., ν_9 (CH stretch), ν_6 (CH wag), and ν_{11} (CH rock) are blue shifted with respect to their gas phase values while the CO stretch (ν_{10}) is red shifted. This trend can be qualitatively explained in terms of a dispersive interaction between the conjugated π electrons of glyoxal with the electrons of the environment. As a consequence, the electron density in the CO bonds decreases which in turn reduces the electron density in the antibonding orbital of the CH groups, which is normally partially occupied in free unperturbed glyoxal. The reduction in electron density strengthens the CH bond

TABLE IX. Infrared absorption frequencies (cm^{-1}) and assignments for glyoxal in Ar, N_2 , and CO matrices at 12 K. The gas phase frequencies and assignments are taken from Ref. 20.

Ar matrix		N_2 matrix		CO matrix		Gas	Assignment
500/1	50/1	500/1	50/1	500/1	50/1		
3450	3450	3460	3872 3455			3895	$\nu_9 + \nu_4$ or $\nu_9 + \nu_8$
3054	3056	3066	3066		3065	3454	$\nu_{10} + \nu_2$
2873	2872	2871				3054	$\nu_{11} + \nu_2$ or $\nu_{10} + \nu_3$
		2865	~ 2864				ν_9 or ν_1 (dimers)
2861	2861						ν_9
2856	2856	2857	2856	2872	2871	2836	ν_1 or ν_9 (in dimers and polymers)
2846	~ 2846	2846	+		+		$\nu_{10} + \nu_4$ or $\nu_{10} + \nu_8$
2834	~ 2834					2799	$\nu_{11} + \nu_3$
2785	2785	2802	2802		2799	2650	$\nu_2 + \nu_6$
2654	2655	2663	2664		2663	2543	$\nu_{11} + \nu_8$ or $\nu_{11} + \nu_4$
		2551	2551	2570		2380	$\nu_7 + \nu_2$
		2389	2390			1872	$\nu_5 + \nu_3, \nu_{11}$ or $\nu_6 + \nu_4, \nu_8$
	1872	1876	1875		1878	1860	ν_{10} (minor sites)
1863	1864	1862	1862		1855		ν_{10}
1732	1732		~ 1747		1745		ν_{10} (dimers + polymers)
1728	~ 1728	~ 1737	~ 1738		1737		?
1724	1724	1731	1730	1728	1727	1730	$\nu_6 + \nu_5$ or ν_3
1723	1723	1729	1728	1725	1725		ν_{11}
1720	1719	1727	+				ν_6 (dimers + polymers)
1717	~ 1717	1721					
1692	1692	1697	1696	1694	1694		
1357	1357		1361		1362		
1317	1317	1323	1323	1321	1321	1312	
			817	818	812		
812	812						
807	807	808	807	808	808	802	ν_6

resulting in a blue shift of ν_6 , ν_9 , and ν_{11} in addition to a slight weakening of the CO bond producing a red shift of ν_{10} . A similar trend has been observed for matrix isolated formaldehyde.²⁹

As shown in Fig. 7 the IR active CH stretch in Ar is split into two components (2861 and 2856 cm^{-1}) with relative intensities which are apparently concentration independent. Furthermore, two weak red shifted features have been observed at 2846 and 2834 cm^{-1} as well as a weak blue shifted band at 2872 cm^{-1} , all of which are concentration dependent.

The major concentration independent absorptions in Ar at 2861 and 2856 cm^{-1} are most probably due to glyoxal in the two different sites, I and II, already apparent from the visible excitation and emission spectra. However, apart from the fact that the relative intensity of the emission from site I with respect to site II is also independent of concentration, no other correspondence between the IR and visible observations has been found. The suggestion of Diem *et al.*²³ that the band at 2861 cm^{-1} might be due to the symmetric CH stretch perturbed into activity by the matrix is considered to be unlikely since this requires that the normally IR inactive symmetric CH stretch (ν_1) be more intense than the IR allowed asymmetric CH stretch (ν_9).

In view of the consistent appearance of a wing at the low frequency side of the CO stretch (ν_{10}) in all matrices at higher concentrations, the CO bond in a dimer or higher aggregate

is considered to be weakened with respect to the CO bond in the monomer. Consequently the CH bond is expected to be strengthened. Thus, the blue wing observed at ~ 1320 cm^{-1} and the band at 2872 cm^{-1} are most likely due to the IR active CH rock (ν_{11}) and CH stretch (ν_9) of glyoxal in a dimer or higher aggregate. Since the symmetry of the molecule is broken in the dimer configuration, the two weak concentration dependent features at 2846 and 2834 cm^{-1} might be assigned to the symmetric CH stretch (ν_1) of glyoxal in a dimer and higher aggregate perturbed into activity. This requires, however, that the relative positions of ν_1 and ν_9 flip between the gas phase and the solid. The alternative is to assign the two weak concentration dependent features of 2846 and 2834 cm^{-1} to the asymmetric CH stretch (ν_9) in a dimer and higher aggregate, respectively, and to assign the band at 2872 cm^{-1} to the symmetric CH stretch (ν_1). This is, however, difficult to reconcile with the behavior of the other vibrations involving the CH bond unless local steric effects play a dominant role for this particular vibration (i.e., the CH stretch). On the basis of the data presented in this paper no decisive answer to this dilemma can be given.

In contrast to the behavior in an argon matrix, no splitting of the CH stretch (ν_9) of the glyoxal monomer was observed in N_2 and CO, in agreement with the absence of emission features attributable to different sites in the visible spectra from those matrices. Weak features in the CH stretching (ν_9) region are also observed in N_2 and CO (see

Table IX for frequencies) and can be similarly explained as those in argon.

The asymmetric CH wagging mode (ν_6) is the only other mode in argon which shows clear evidence for two sites. No confusion with the symmetric CH wag (ν_8) is possible since ν_8 is located at 1048 cm^{-1} in the gas phase. In argon, however, the relative intensity seems dependent on concentration. This may be an artifact since it is a difficult region to work in because of the severe broadening in the 50/1 case.

B. Absorption and excitation spectra

Since the correct assignment of the excitation spectra, in particular the 0_0^0 transition, is of key importance in the interpretation of the fluorescence and phosphorescence spectra, the arguments supporting this assignment are enumerated here. First, the intensity distribution of the excitation spectrum in argon is very similar to the intensity distribution in the gas phase excitation spectrum³⁰ from which the hot bands have been removed. Second, the vibrational spacings with respect to the 0_0^0 band in the gas phase closely match those in argon. Third, the experiments in which Coumarin 2 was used ($\lambda_{\text{ex}} = 431\text{--}475\text{ nm}$), clearly show no additional peaks in the excitation spectra at wavelengths longer than 459.9 nm (site I) and 461.6 nm (site II). Fourth, in N_2 and CO , the most intense peak, which was assumed to be 0_0^0 transition, was always at the red end of both the excitation and absorption spectra.

The visible absorption and excitation spectra are also characterized by several trends. The shift in position of the 0_0^0 transition with respect to the gas phase changes from a red shift in argon to a blue shift in N_2 and CO . Parallel to this behavior is the observation of broadening of the absorption and emission features in the order Ar , N_2 , CO . In connection with this, it is interesting to note that the hard sphere diameter of glyoxal, estimated to be $\sim 0.4\text{ nm}$,¹⁴ is comparable to the substitutional site diameter of 0.376 nm in an argon matrix.³¹ This suggests that sites I and II correspond to glyoxal in disubstitutional and monosubstitutional sites, respectively. This explanation is consistent with the appearance of sharp zero phonon lines in site I and the absence of zero phonon lines in site II because stronger coupling to the phonon bath is expected in the monosubstitutional site. The overall red shift of the 0_0^0 transition in argon with respect to the gas phase is then explained by the dispersive interactions (proportional to the polarizability) between glyoxal and its environment. Since the diameters of the cylindrical sites in N_2 and CO are 0.342 and 0.348 nm , respectively,³¹ the blue shift of the 0_0^0 transition in N_2 and CO can be induced by the repulsive part of the interaction between the conjugated π system of glyoxal and the electrons of the environment. In this case, glyoxal is assumed to be predominantly trapped in a set of distorted monosubstitutional sites. The broadening of the bands in N_2 and CO , which indicate strong interactions, supports this picture. A similar trend has been observed for the $^2A''(\Pi) \leftarrow ^2A'$ transition of matrix isolated HCO .²⁴

C. Emission spectra

The interpretation of the fluorescence spectra, assigned to the $\tilde{A}^1A_u \rightarrow \tilde{X}^1A_g$ transition, is complicated by several observations. The first rather puzzling result is the absence of the 0_0^0 transition in the fluorescence spectra. Second, the excitation spectra in argon show features associated with site I blue shifted with respect to those associated with site II, while in the fluorescence spectra these relative positions are reversed. Consequently, no simple explanation of the shifts in terms of stabilization of one of the particular electronic states due to environmental effects is suitable. Two different hypotheses have been considered to account for these observations and will be discussed in turn. The first is emission from an excited vibrational level in the $\tilde{A}^1A_u$ and $\tilde{a}^3A_u$ state and the second is exciplex formation of glyoxal with its neighboring atoms or molecules resulting in the breakdown of selection rules. The former suggestion cannot account for all of the observations while the latter can.

At first, invoking emission from a long-lived excited vibrational level in the $\tilde{A}^1A_u$ state seems attractive. Indeed, the vibrational spacings in the emission spectra from site I and site II can be explained assuming the main emission bands at 468.0 and 492.2 nm to be due to the dominant gas phase 8_1^1 and 8_2^1 transitions, respectively, and the bands at 464.6 and 488.4 nm to be due to $8_1^1 7_1^1$ and $8_2^1 7_1^1$ transitions, respectively, while combination bands would explain the weaker features in the spectra. The levels 8^1 and $8^1 7^1$ would have to act as effective traps, preventing molecules from reaching the ground vibrational level in the 1A_u state by vibrational relaxation, thereby rationalizing the absence of the 0_0^0 transition. Problems arise, however, with the excitation spectrum from site II. In this picture, the spectrum from site II has to be interpreted in its entirety as a hot band excitation spectrum (normally forbidden by selection rules) possibly from level 7_1 in the ground state, which implies substantial population of this level, which lies 127 cm^{-1} above the 0_0 level, in a matrix at 12 K . Another important reason to reject this explanation is the observation of an unaltered site I emission spectrum when the lowest vibrational level in the $\tilde{A}^1A_u$ state is excited directly at 460.0 nm . "Up relaxation" from the lowest vibrational level in the $\tilde{A}^1A_u$ state to the 8^1 level is considered to be impossible. Therefore, to explain the observations, a two-step excitation process would have to be invoked, in which, after fluorescence, glyoxal remained vibrationally excited in the $\tilde{X}^1A_g$ state long enough to be excited again. The latter mechanism was excluded in experiments in which no change in relative fluorescence intensity was observed with laser repetition rates varying between 1 and 0.01 Hz . In addition direct two-photon processes were excluded by experiments, in which a linear rather than quadratic relationship was found between laser intensity and fluorescence intensity. Finally, similar observations found for the $\tilde{a}^3A_u \rightarrow \tilde{X}^1A_g$ phosphorescence would require lifetimes for nonradiative vibrational relaxation of the 8^1 and $8^1 7^1$ levels in the excited $\tilde{a}^3A_u$ state to be in the millisecond domain which seems highly unlikely.

The second hypothesis requires assigning all vibrational spacings associated with site I using mode 12 in the ground state (asymmetric CCO bend) in combination with the tran-

FIG. 8. Simplified energy level diagram of glyoxal in sites I and II in an argon matrix. If all fluorescence bands are combined with 12_1 in site I and with 7_1 in site II the reversed relative positions of the features associated with sites I and II in the fluorescence and excitation spectra can be achieved.

sitions usually observed for gas phase glyoxal from the lowest vibrational level of the $\tilde{A}^1A_u$ state¹⁷ (Table IV). The emission spectrum from site II is then possible to explain by invoking mode 7 (torsional vibration) in combination with the normal gas phase transitions (Table IV). Figure 8 drawn, using this hypothesis, shows a schematic energy level diagram which demonstrates how the relative positions, of features due to sites I and II, in the excitation and fluorescence spectra are reversed. To account for this behavior, the following model is proposed. When glyoxal is excited into the $\tilde{A}^1A_u$ state, the electron cloud of the molecule is enlarged to the extent that an excited state complex (exciplex) with one or more of the neighboring argon atoms is formed. Consequently, because the equilibrium position of the nuclei of glyoxal in the exciplex is distorted and different from that of the $\tilde{A}^1A_u$ state of the free molecule, the Franck–Condon factors for the $\tilde{A}^1A_u \rightarrow \tilde{X}^1A_g$ emission process are therefore considerably altered. When the molecule relaxes, the complex dissociates and $\tilde{X}^1A_g$ glyoxal is born vibrationally excited due to the much faster rearrangement of the electrons than the nuclei (Born–Oppenheimer approximation). The relaxation of the exciplex geometry to the ground state geometry in sites I and II, then, favors excitation of modes ν_{12} (asymmetric CCO bend) and ν_7 (torsion), respectively. Due to the change in equilibrium configuration of the nuclei the Franck–Condon factor for the 0_0^0 transition in the emission spectra of sites I and II vanishes. In addition to accounting for the transitions, this model is consistent with fast vibrational relaxation in the excited state, in agreement with the observation that the emission spectra do not change as a function of excitation wavelength. The appearance of the 0_0^0 transition in the excitation and absorption spectra can also be well understood, because the ground state glyoxal molecule in the matrix is *not* perturbed strongly, and has approximately the same planar equilibrium configuration as in the gas phase, since the rule of mutual exclusion still holds as

shown by the IR spectra. The Franck–Condon factors in the absorption process are therefore not influenced strongly, which again can be understood in terms of the Born–Oppenheimer approximation.

The vibrational frequencies in the ground state of ν_{12} in site I and ν_7 in site II, which are assumed to be preferentially excited in the emission process, can be calculated from each of the vibronic transitions observed. Using the gas phase vibrational frequencies in the ground state for ν_2 , ν_3 , ν_4 , ν_5 , and ν_8 in combination with the measured 0_0^0 transitions in sites I and II, the average value of ν_{12} is found to be $349 \pm 20 \text{ cm}^{-1}$ in site I while $\nu_7 = 116 \pm 17 \text{ cm}^{-1}$ in site II. These values agree with the gas phase frequencies in Table III within the error bars.

The rather tight fit of glyoxal in the substitutional sites in the matrices studied, as previously discussed in Sec. IV B, might provide the basic requirement for the complex formation observed in this molecule. A picture of the geometry of the different exciplexes can partially be provided by the specific perturbations observed in the spectra. The geometry of site II apparently induces activity in mode 7 (the torsional vibration), suggesting that the argon atom in the exciplex is seated above or below the plane of the molecule distorting the planar geometry. The geometry of site I favors mode 12 (the asymmetric CCO bend) activity suggesting that an argon atom in the plane of the molecule participates in the exciplex.

Interesting corroborative evidence supporting the hypothesis involving exciplex formation is provided by the study of glyoxal complexes formed in supersonic expansion experiments.^{18,19} The glyoxal–argon gas phase complex, in which the Ar is assumed to be seated above the plane of the molecule, also shows that mode 7 is perturbed into activity. The 7_1^0 emission line of the complex was observed as well as various combination bands.

Diem *et al.*²³ also measured laser-induced fluorescence from glyoxal in an argon matrix, though, only emission from site I was observed. The interpretation of the fluorescence spectrum by these authors is contradictory to the one described above. They assigned the fluorescence peak at 467.5 nm to the 0_0^0 transition and, consequently, the band at 491.0 nm to the 8_1^0 transition, but they simultaneously showed an absorption spectrum, very similar to the one reported here (Fig. 2), in which the 0_0^0 transition is clearly located at 460.0 nm. Therefore the assignment of the band at 467.5 nm to the 0_0^0 transitions seems to be incorrect.

Unambiguous assignments of the vibronic transitions in the phosphorescence spectra (Table V) are more difficult to make because the 0_0^0 position of the $\tilde{a}^3A_u \rightarrow \tilde{X}^1A_g$ transition is not evident from the absorption of excitation spectra. Nevertheless, very similar shifts in wavelength are observed, which reverse relative position for sites I and II depending upon whether an excitation or phosphorescence spectrum is measured. This behavior is similar to that found with the fluorescence spectrum from sites I and II. As before, it is not possible to make a straightforward interpretation in terms of the stabilization of one of the electronic states involved. Building on the hypothesis of the formation of an exciplex as presented above, the vibrational spacings in the spectrum

can be explained using mode 12 in site I and mode 7 in site II. While it may seem contrived that both the singlet and triplet states form a similar exciplex, this model is supported by the similarity in electronic structure of the excited $\tilde{A}^1A_u$ and $\tilde{a}^3A_u$ states, which both have the electron promoted into the nonbonding (a_u) π^* orbital.³ After formation of the exciplex in the $\tilde{A}^1A_u$ state only a spin flip is required for intersystem crossing, leaving the structure of the electronic orbitals unchanged and, consequently, dissociation of the complex would not be expected.

Another point to consider is the difference in electronic energy between the 0^0 levels of the $\tilde{A}^1A_u$ and $\tilde{a}^3A_u$ states. Since both have the same electronic structure, the stabilization energy for both states in the matrix is expected to be approximately equal. In the gas phase, the $\tilde{A}^1A_u$ state is $21\,969\text{ cm}^{-1}$ and the $\tilde{a}^3A_u$ state is $19\,196\text{ cm}^{-1}$ above the ground state; a difference of 2773 cm^{-1} (Ref. 31). In an argon matrix only the electronic energy of the $\tilde{A}^1A_u$ state is known. It is $21\,739\text{ cm}^{-1}$ for site I and $21\,654\text{ cm}^{-1}$ for site II (see Table II). The 0^0 level of the $\tilde{a}^3A_u$ state is therefore calculated to be at $18\,966\text{ cm}^{-1}$ (527.2 nm) in site I and $18\,881\text{ cm}^{-1}$ (529.6 nm) in site II. Adopting these values as the electronic origin of the $\tilde{a}^3A_u \rightarrow \tilde{X}^1A_g$ transition for sites I and II, combination bands with ν_{12} in site I and ν_7 in site II are indeed found to fit the observed frequencies; again supporting the exciplex picture, this time with the excited triplet state. The calculated wavelengths in Table V are based on the electronic origins determined above and the vibrational assignments given. Gas phase ground state vibrational frequencies (Table III) were used except those for ν_7 and ν_{12} for which the previously determined average values have been taken (i.e., $\nu_7 = 116 \pm 17\text{ cm}^{-1}$ and $\nu_{12} = 349 \pm 20\text{ cm}^{-1}$).

The assignments of the bands in the fluorescence and phosphorescence spectra in N_2 and CO matrices pose similar problems to those encountered in argon. Again no emission has been observed at the 0^0_0 position determined from the absorption and excitation spectra. Using the framework provided by the explanation of the spectra in argon, this behavior can be accounted for by assuming the formation of an exciplex of glyoxal with one or more of the host molecules. In nitrogen as well as in CO the fluorescence spectrum can be explained in terms of combination bands of the normally active transitions involving the 0^0 level in gas phase glyoxal¹⁷ with a transition, called x_y^0 , induced by the formation of an exciplex (see Table VI). The mean value of the vibrational spacing corresponding to the x_y^0 transition is found to be $698 \pm 35\text{ cm}^{-1}$ in a N_2 matrix and $1028 \pm 35\text{ cm}^{-1}$ in a CO matrix.

The rather large values of these vibrational spacings involved in N_2 and CO matrices compared to those in argon ($\nu_7 = 116 \pm 17\text{ cm}^{-1}$ and $\nu_{12} = 349 \pm 20\text{ cm}^{-1}$) indicate strong interactions consistent with the conclusions drawn from the blue shift and breadth of the features in the absorption and excitation spectra. An unambiguous assignment for the x_y^0 transitions cannot be given; however, in a nitrogen matrix the most likely candidates are the 12_2^0 ($\Delta E_{\text{gas}} = 678\text{ cm}^{-1}$) and the $5_1^0 7_1^0$ ($\Delta E_{\text{gas}} = 677\text{ cm}^{-1}$) transitions and in a CO matrix, the 4_1^0 ($\Delta E_{\text{gas}} = 1065\text{ cm}^{-1}$) and the 8_1^0

($\Delta E_{\text{gas}} = 1048\text{ cm}^{-1}$) transitions.

Further corroborative evidence of the exciplex model holding in N_2 and CO matrices as well is provided by the explanation it allows of the phosphorescence spectra. As discussed above, the stabilization energy for the $\tilde{A}^1A_u$ and the $\tilde{a}^3A_u$ states is expected to be nearly equal in a given environment. Therefore the electronic energy of the $\tilde{a}^3A_u$ state (in wave numbers) above the ground state can be calculated using the 0^0_0 of the $\tilde{A}^1A_u \rightarrow \tilde{X}^1A_g$ transition and the energy difference between the $\tilde{A}^1A_u$ and the $\tilde{a}^3A_u$ states in the gas phase. Consequently, in a nitrogen matrix, the electronic origin of the $\tilde{a}^3A_u$ state is found to be at $19\,350\text{ cm}^{-1}$ (516.8 nm) and in a CO matrix $19\,399\text{ cm}^{-1}$ (515.5 nm). Using these values, the phosphorescence spectra in both matrices can be satisfactorily explained with combination bands involving the previously determined x_y^0 transitions (see Table VII). The success of this explanation strongly supports the model of exciplex formation in the triplet state. Breukelaar has pointed out (private communication) that energy levels invoking only certain multiplets of ν_7 instead of ν_7 and ν_{12} , can also be used to reproduce the observations. For example, $3\nu_7$ (348 cm^{-1}) is comparable to ν_{12} (339 cm^{-1}), $6\nu_7$ (696 cm^{-1}) is comparable to the value found for x_y^0 in N_2 (698 cm^{-1}), while $9\nu_7$ (1044 cm^{-1}) is comparable to the value in CO (1028 cm^{-1}). However, the absence of evidence for other multiplets of ν_7 contributing to the spectrum argues against an explanation involving only ν_7 .

D. Lifetimes and quantum yields

Fluorescence and phosphorescence lifetimes have been measured in all matrices and are listed in Table VIII. These lifetimes, in combination with the ratio of the integrated intensities of fluorescence to phosphorescence (I_f/I_p), permit the extraction of detailed information on the deexcitation processes in matrix isolated glyoxal.

The relaxation processes considered after excitation into the 0^0 level of the $\tilde{A}^1A_u$ state are fluorescence, internal conversion to the ground state, and intersystem crossing to the $\tilde{a}^3A_u$ state possibly followed by phosphorescence. The quantum yields of these processes are defined as ϕ_f , ϕ_{ic} , ϕ_{isc} , and ϕ_p , respectively.

In the gas phase, the radiative lifetimes for the $\tilde{A}^1A_u(0^0)$ and $\tilde{a}^3A_u(0^0)$ states are $\tau_{fg} = 4.1\text{ }\mu\text{s}$ ³⁰ and $\tau_{pg} = 3.29\text{ ms}$ ¹⁶, respectively. In a classical dielectric, these values will be altered by two separate effects as discussed previously by several authors.^{32,33} The first is caused by short-range interactions with nearest neighbors resulting in a change of the transition dipole of the molecule. The second effect, which is usually much larger, is caused by the increase of the radiation field density of states, caused by the index of refraction of the solvent.

The latter correction is commonly given as $(\tau_s)^{-1} = n_s \{ (n_s^2 + 2)/3 \}^2 (\tau_g)^{-1}$ in which n_s is the index of refraction of the solvent, τ_s is the radiative lifetime expected in the solvent, and τ_g is the radiative lifetime in the gas phase.³² This correction factor, derived from the Lorentz-Lorenz dielectric model overestimates the increase of $(\tau)^{-1}$ by about a factor of 2.³³ Taking this into account, the radia-

tive lifetime of the $\tilde{a}^3A_u(0^0)$ state is expected to be ~ 2.25 ms in argon and CO ($n_s = 1.29$) and ~ 2.22 ms in nitrogen ($n_s = 1.30$). The radiative lifetime of the $\tilde{A}^1A_u(0^0)$ state is assumed to be $\sim 2.8 \mu\text{s}$ in all three matrices.

The calculation of the fluorescence and phosphorescence quantum yields (ϕ_f and ϕ_p) in these matrices requires knowledge of the pure radiative lifetimes of the complex in the gas phase which, unfortunately, is not available. Therefore, to investigate the effect of exciplex formation on the deexcitation channels of $\tilde{A}^1A_u$ and $\tilde{a}^3A_u$ glyoxal, we use the radiative lifetimes of the "free" gas phase molecule to calculate the *effective* quantum yields. Halberstadt and Soep¹⁹ use a similar approach to calculate the lifetime of intersystem crossing in the Ar-glyoxal gas phase complex. Adopting the values presented above, ϕ_f and ϕ_p have been determined using $\tau_m = \phi\tau_s$, in which τ_m represents the radiative lifetime measured for matrix isolated glyoxal (Table VIII). Only an upper limit of the fluorescence quantum yield can be given this way, since the fluorescence lifetime was shorter than the experimental time resolution (45 ns).

The ratio I_p/I_f has been determined as well, by integrating over the entire fluorescence or phosphorescence spectra and correcting for spectral sensitivity, amplifier gains, and time scales. Using this ratio, the quantum yield for intersystem crossing can be calculated from $I_p/I_f = \phi_{isc}\phi_p/\phi_f$. Thus, the values of ϕ_{isc} given in Table VIII are proportional to the fluorescence quantum yield and are therefore only upper limits. Similar considerations hold for ϕ_{ic} since it is defined as $\phi_{ic} = 1 - \phi_{isc} - \phi_f$ and therefore only lower limits can be given. Nevertheless appreciable changes in the ratio I_p/I_f are observed which suggest matrix dependent branching ratios with intersystem crossing substantially more favored in a nitrogen matrix than in CO.

In general the decrease in fluorescence quantum yield from 0.58 for the 0_0^0 transition of gas phase glyoxal³⁰ to ≤ 0.02 in the matrix shows the importance of the nonradiative decay channels of the $\tilde{A}^1A_u$ state both to the $\tilde{a}^3A_u$ and ground state. Both accepting states offer a quasicontinuum of final states comprised of the closely packed molecular vibrational levels in combination with the phonon bath states. Only weak temperature dependence of the ratio I_p/I_f has been found in all three matrices. Varying the temperature from 12 to 31 K increased I_p/I_f by a factor of ~ 1.2 . Consequently, localized phonon modes, mainly determined by strong short-range interactions and local symmetry, are most likely responsible for the interaction rather than coupling to the phonon bath of the matrix. This behavior is consistent with exciplex formation.

V. CONCLUSIONS

The analysis of laser-induced fluorescence and phosphorescence as well as absorption and excitation spectra of glyoxal in Ar, N₂, and CO matrices, shows that it forms an exciplex with its nearest neighbors in both the $\tilde{A}^1A_u$ and $\tilde{a}^3A_u$ states. The distorted equilibrium configuration of the nuclei in the exciplex results, after fluorescence or phosphorescence, in a ground state glyoxal molecule born vibrationally excited. The emission spectra measured in all three matrices, therefore, differ dramatically from the gas phase

spectrum available in the literature. In argon, the fundamentals ν_{12} and ν_7 are preferentially excited, in sites I and II, respectively, and are found in combination with the gas phase transitions, usually observed. In N₂ and CO matrices an unambiguous assignment for the preferentially excited modes cannot be given. The fact that no 0_0^0 emission is found in the fluorescence spectra while the 0_0^0 transition is strong in absorption and that the rule of mutual exclusion still holds in the IR, are in agreement with the formation of an excited rather than a ground state complex. Fluorescence and phosphorescence lifetimes place limits on the quantum yields of the various deexcitation channels and shows that localized phonon modes play a dominant role in coupling to the matrix.

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