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Below excitation energies of 22 500 cm^{-1} biacetyl behaves as a small molecule as evidenced by the pressure dependence of its phosphorescence and the structure of the excitation spectrum. The sudden transition to large (statistical) molecule behavior at this energy can be explained by the presence of a ^3B_g state for which there is also theoretical evidence.

I. INTRODUCTION

In a previous paper[1] we discussed the electronic states of biacetyl, coming to the conclusion that the original interpretation of McClure and Sidman[2] is probably erroneous with respect to the ^1B_g and ^3B_g assignments. Since, however, direct absorption to ^1B_g and ^3B_g from the ground state is symmetry forbidden, detection in this conventional way is very difficult. Thinking about radiationless transitions, one might expect that the close-lying ^3B_g state might influence the radiationless singlet to triplet process drastically and consequently the fluorescence and phosphorescence behavior. Furthermore, Parmenter and Poland[3] pointed out that the biacetyl seemed to behave paradoxically in the sense that their semiempirical calculations showed small-molecule behavior at 4358 Å excitation, while when actually exciting with the 4358 Å Hg line the experiment clearly showed large-molecule behavior i. e., pressure-independent fluorescence and phosphorescence yields. It thus seemed useful to measure fluorescence (Y_F) and phosphorescence yields (Y_P) as a function of the excitation wavelength and as a function of pressure in gaseous biacetyl. In this paper we show that the existence of the ^3B_g state and the paradoxical large-molecule behavior intimately related to each other.

II. EXPERIMENTAL CONDITIONS AND COMPLICATIONS

Essentially the same experimental setup has been used as previously published.[4] The exciting light from a 200-W Xe high-pressure arc was passed through a Hitachi monochromator and admitted into the cell via a quartz window. The fluorescence and phosphorescence were detected by a Philips U. V. P. 150 photomultiplier via a variable interference filter (Schott) together with suitable Corning filters and lenses. Experimental conditions (i. e., filter, amplification, etc.) were always chosen in such a way that no signal could be detected without the presence of biacetyl. A "base line" for all experiments could therefore be continuously re-established by pumping out the biacetyl. The measure-

ments were performed at a temperature of 10–15 °C. Biacetyl (Merck) was purified, degassed, and dried in the usual manner. Gas-chromatographic analyses showed the purity to be higher than 99. 9%. The emission intensities were measured by monitoring the fluorescence and phosphorescence at a fixed detection wavelength (5150 Å, bandpass 160 Å). The following complications now arise:

(i) Since at the excitation wavelength employed here it is very difficult to measure the fluorescence at a wavelength for which the phosphorescence signal is zero (at ~ 4600–4650 Å), the fluorescence and phosphorescence signals cannot be measured separately in any direct way.

(ii) Since the fluorescence and phosphorescence intensities are measured at a single wavelength in the fluorescence or phosphorescence spectrum, no total yields are measured.

(iii) Emission from long-lived species (i. e., triplet emission) may suffer a wall effect because we are measuring a solid angle of 4π (spherical cell).

Ad i. It is known that the phosphorescence is strongly quenched by adding small amounts of oxygen (half-pressure value ~ 0. 02 mm[5]), while the fluorescence is not otherwise affected by O_2 than for example by N_2. In Fig. 1 a Stern–Volmer plot is given of the total signal measured against the O_2 pressure. It was found that at an initial biacetyl pressure of 1. 0 mm an oxygen pressure of 1. 4 mm is sufficient to suppress a measurable phosphorescence signal. The initial signal of the biacetyl–O_2 mixture is time independent for at least $\frac{1}{2}$ h, indicating that a reaction of the biacetyl with O_2 is not affecting the results seriously during the time of a typical quenching experiment (20 min). This method thus allows the fluorescence and phosphorescence signals to be separated completely.

Ad ii. The validity of using single-wavelength detection regions rests on the assumption that the spectral distribution of both the singlet and triplet emission remains invariant under different condi-
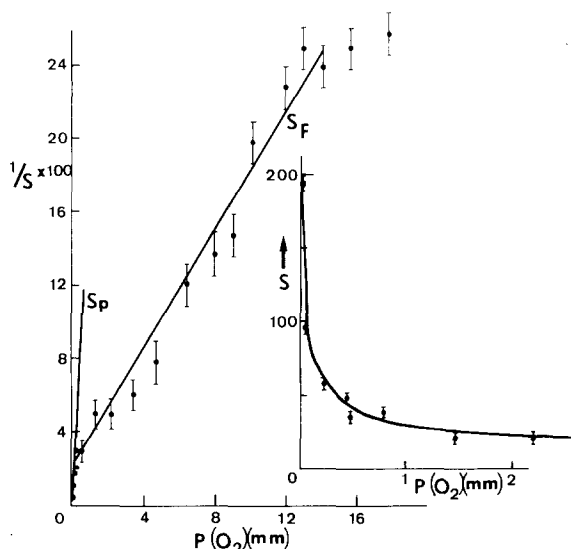
FIG. 1. Stern–Volmer plot of the total signal illustrating that it is composed of phosphorescence (very effectively quenched by O_2) and fluorescence (much less effectively quenched). Excitation–wavelength 4540 Å (bandwidth 30 Å). The inset shows the very low–pressure behavior of the total signal. All units are arbitrary.

tions (i.e., pressures and excitation wavelength). We have tested this point explicitly by repeating the experiments at different detection wavelengths. It appears that the fluorescence and phosphorescence spectra (bandpass 160 Å) are invariant under various conditions of pressure and excitation wavelengths. Thus, except for the emission from long-lived species (see next paragraph), the measured *signals* (S) are proportional to the respective *yields* (Y), where the proportionality constant is determined by an experimental geometry factor and the absorption coefficient.

Ad iii. Suppose we have a triplet species with a mean lifetime of 2 msec at lowest pressures; within this lifetime the molecules may diffuse about 1 cm at 0.5 mm pressure. Thus, with a cell diameter of 20 cm a fraction of $\approx 15\%$ of the molecules will diffuse to the walls. If we assume every collision with the walls to be effective in deactivation of the excited species one would observe a trivial increase of $\approx 15\%$ in the phosphorescence in going from the low pressure to high pressures (≈ 10 mm) where diffusion to the walls is neglible. Since it is difficult to correct theoretically[3] for the wall effect (diffusion coefficient, probability factor for wall de-activation) we made use of the experimental results of Parmenter and Poland[3] and Sidebottom *et al.*[6] which fortunately conclusively demonstrate that the phosphorescence yield (Y_p) at 4358 Å excitation is independent of pressure from

0.03 to 40 mm Hg. Thus, we use the measurements at 4358 Å excitation as a reference, assuming that the wall deactivation at 4358 Å is the same as for the other excitation wavelengths, which is, of course, a plausible assumption, because the vibrational relaxation in the triplet manifold is much faster than the phosphorescence lifetime (as appears from the independence of the phosphorescence spectrum on pressure) and thus wall deactivation always occurs from the vibrationless triplet level. As is expected no wall correction needs to be applied for the fluorescence since the lifetime of the singlet species is about 10^{-8} sec, a possible correction would amount to less than 0.01%. Thus, after application of the wall effect correction on the phosphorescence signals these signals are proportional to the respective yields (Y) (i.e., they are relative quantum yields) with again a proportionality constant determined by the experimental geometry factor and the absorption coefficient.

Still one remark has to be made about the method of examining the pressure dependence of the fully corrected signals: the biacetyl pressure was kept constant and the system was then pressurized by the addition of a foreign gas (N_2, O_2, hexane). [Hexane was also used as a foreign gas and the same effects as with N_2 were also observed. Therefore and because of the high quality (99.997%) of the N_2, for the discussion we always refer to the N_2 measurements.] We now have to assume that the absorption coefficient does not change with pressure to replace the signals by the respective relative yields. Fortunately, the experiments indicate that this assumption is confirmed: Fig. 2(a) gives S_P (corrected) as a function of N_2 pressure for excitation at 4540 Å (22 025 cm^{-1}) while Fig. 2(b) gives S_F as a function of pressure at the same excitation wavelength. If the pressure effect would be simply due to a change in absorption, we would expect the same effects (i.e., an increase or a decrease) in both S_P and S_F. *We can conclude that we may safely replace the corrected fluorescence and phosphorescence signals by the respective relative yields.*

III. RESULTS

Figure 3 shows the phosphorescence excitation spectrum (bandpass 5 Å) at a biacetyl pressure of 1.0 mm and with N_2 at a pressure of 20 mm. The spectrum has been corrected for lamp intensity. The insert shows the excitation spectrum for biacetyl-d-$_6$ between 4570 and 4470 Å. Since the absorption spectrum of biacetyl (Fig. 4)[7] is completely diffuse in this excitation range the structure must be due to changes in the phosphorescence yield.

Table I collects the ratios Y_P(20 mm)/Y_P(1 mm) at various wavelengths of interest. A similar col-
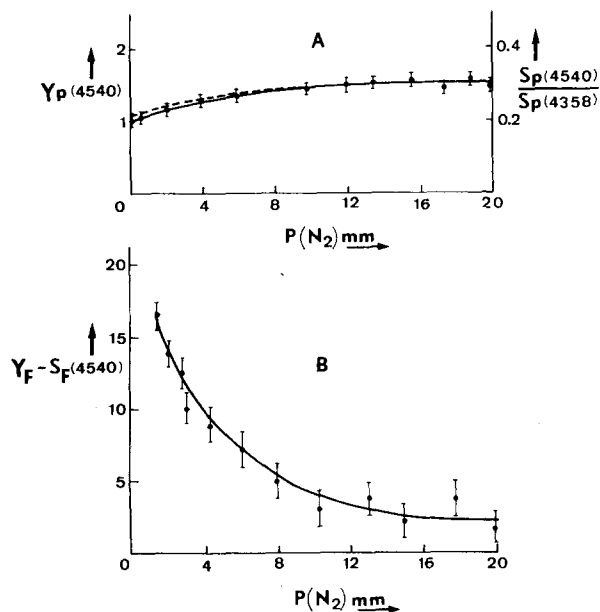
FIG. 2. (a) Typical pressure behavior of the relative phosphorescence yield. The dotted line gives the relative total light output. Biacetyl pressure 1 mm. Excitation wavelength 4540 Å (30 Å). (b) Typical pressure dependence of the fluorescence signal (yield). Biacetyl pressure 1 mm., 1.4 mm. O_2 added. Excitation wavelength 4540 Å (30 Å). The units of $S_F(Y_F)$ are arbitrary.

lection of Y_F/Y_P at 1.0 mm. is given in Table II. As pointed out above, the measurements of the fluorescence signal necessitated the pressure of 1.4 mm of O_2 and 1 mm biacetyl. For the ratios Y_F/Y_P the results (averaged over five measurements) were extrapolated back (Stern–Volmer Fig. 1) to 0 mm O_2 (N_2) and 1.0 mm biacetyl.

In general, the *ratio of the corrected signals* is not an absolute measure for the *ratio of the yields*. However, detecting at 5150 Å (bandpass 160 Å), $S_F(corr)/S_P(corr)$ is accidently equal to Y_F/Y_P at 4358 Å (22 990 cm^{-1}) excitation; cf. our ratio $S_F(corr)/S_P(corr) \approx 2\% \pm 0.5\%$ with Y_F/Y_P calculated from the integrated yields: 1.7%.[8] Also, since with the fairly wide detection bandwidth (160 Å) we did not find a significant change in the phosphorescence and fluorescence spectra at different excitation wavelengths we made only minor errors, if we replaced $S_F(corr)/S_P(corr)$ by Y_F/Y_P for all wavelengths in this particular case.

IV. DISCUSSION

A. The location of the ^3B_g state

From the three different regions of the excitation spectrum we can immediately surmise that the following three processes take place:

(a) ~20 000–21 500 cm^{-1} direct absorption to the triplet state (pressure independent S_P).

(b) ~21 500–22 500 cm^{-1} excitation to a singlet state (pressure dependent S_P).

(c) $\gtrsim$22 500 cm^{-1} excitation to higher vibronic components of the same (b) or a different electronic state (pressure independent S_P).

Both the energy range and the pressure independent of S_P indicate that region (a) corresponds to direct excitation of the triplet of biacetyl. Since vibrational relaxation in the triplet manifold is much faster than the phosphorescence lifetime, no effect of pressure is observed. From the totally different pressure behavior in regions (b) and (c) it can immediately be concluded that there is a sudden change of character of the radiationless $S \rightarrow T$
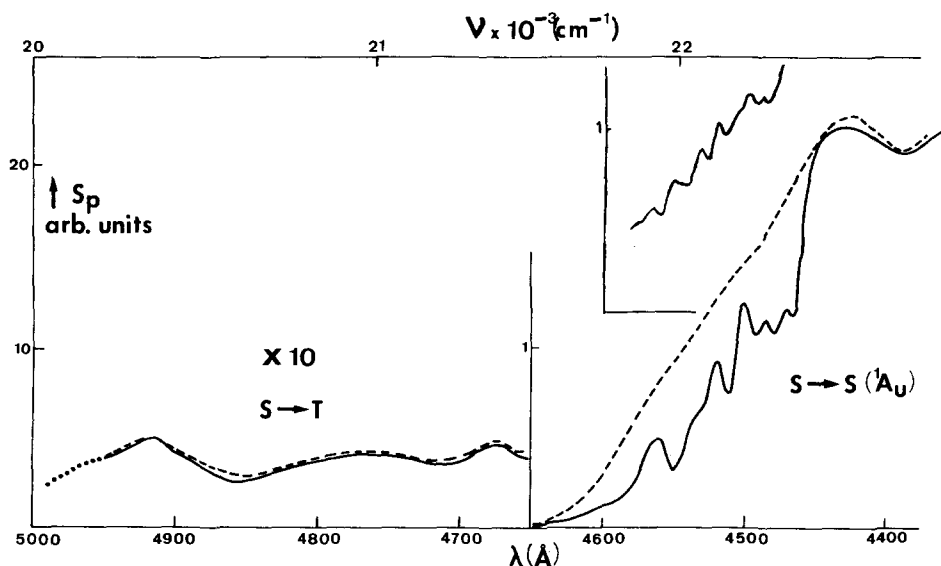
FIG. 3. The phosphorescence excitation spectrum of biacetyl. Solid line at a pressure of 1 mm, dotted line at a pressure of 20 mm of N_2 added. The excitation bandwidth was 5 Å in the $S \rightarrow S$ range and 20 Å in the $S \rightarrow T$ range. The insert shows the spectrum for biacetyl-d_6 between 4470 Å and 4570 Å (same units). The spectrum at $\approx$ 5000 A is somwhat uncertain, because of stray light problems. The 0–0 is probably located at about 5000 Å.

TABLE I. The increase of the phosphorescence signal going from 1 mm biacetyl to (1 mm biacetyl + 20 mm N_2) at different excitation energies.

Excitation energy (bandwidth 30 Å)	Y_p (20 mm)/Y_p (1 mm)
4670 Å (21 410 cm^{-1})	1.0
4600 Å (21 740 cm^{-1})	2.0
4575 Å (21 850 cm^{-1})	2.6
4540 Å (22 025 cm^{-1})	1.5
4530 Å (22 075 cm^{-1})	1.4
4358 Å (22 900 cm^{-1})	1.0

process. Of course, the sharp division between the two wavelength regions is somewhat smeared out by hot band excitations.

In the region (b) the molecule behaves like a small molecule because the phosphorescence yield depends on the pressure, $t_{exptl} \gtrsim \hbar\rho$ at low pressures, where ρ is the effective density of triplet vibronic states. At higher pressures the recurrence time is increased by external collisional interactions and as a consequence Y_P increases while Y_F decreases with pressure. In region (c), where Y_P and Y_F are pressure independent, biacetyl behaves like a large molecule, $t_{exptl} \ll \hbar\rho$; external collisions do not affect this condition.

If the sudden change of behavior of biacetyl at about 22 500 cm^{-1} would have to be explained in terms of only two electronic states: ^1A_u (~21 850 cm^{-1}, maximum pressure dependence) and ^3A_u
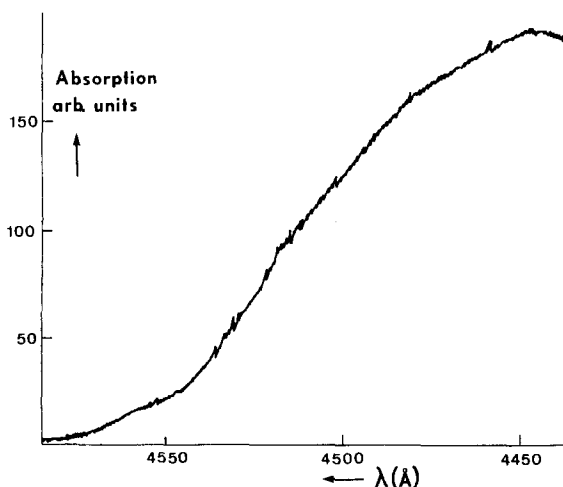

FIG. 4. Absorption spectrum of biacetyl-h_6 at 0.2 mm (path length 120 m). The very weak structure in this spectrum is well above the noise level and different for the deuterocompound. (We are very grateful to Dr. G. Fischer for his cooperation in measuring this spectrum.)

(~20 000 cm^{-1}) an unrealistically sudden increase of a factor of 30 or more[2] in $\rho\overline{F}$ (where ρ is the density of triplet vibronic states and $\overline{F}$ is the average Franck–Condon factor) would have to be assumed in going from zero–zero excitation to about 500 cm^{-1} above zero–zero.

For some systems the dependence of $\rho\overline{F}$ on the energy gap is known empirically[9]; it is often roughly exponential with a small exponent. For example, for benzene the increase of $\rho\overline{F}$ over an energy range of 2000 cm^{-1} is only 1.9.[10] For β-naphtylamine this increase is only a factor of 2 over an energy-range of 1000 cm^{-1}.[11] The total density of triplet vibronic states in biacetyl increases at most by a factor of 4–10[12] from 21 850 to 22 500 cm^{-1}. Since the Franck–Condon factor is expected to decrease, an increase in $\rho\overline{F}$ of a factor 2–3 seems to be all that can be expected on a two electronic state model. However, an increase by a factor of 2–3 certainly cannot explain the rapid change from a small-molecule limit into a large-molecule limit.

When we add this new paradox to the already existing one concerning the large-molecule behavior at 4358 Å (22 990 cm^{-1}) excitation, we are naturally forced to consider the effects of a third or perhaps a fourth electronic state, which might be involved in the $S \rightarrow T$ radiationless process. The obvious candidates for these states are the ^3B_g and perhaps the ^1B_g state. As has been indicated before,[2] it is very likely that either the ^3B_g(I) or the ^3B_g(II) state is located near the ^3A_u(I) state. We therefore have to consider a three-level diagram consisting of a singlet (^1A_u), a lower triplet (^3A_u), and a higher triplet (^3B_g). In the following, we will give two reasons why the sudden change of behavior then comes about:

(i) The mixing of the states. Because the ^3B_g state is much closer to the ^1A_u state than the ^3A_u state, the former states will mix strongly. An estimate of the coupling enhancement $^1A_u \leftrightarrow {}^3A_u$ via the ^3B_g state yields a factor ~5.[12,13] If the lower manifold ^3A_u would be statistical the $^1A_u \rightarrow {}^3A_u$ radi-

TABLE II. The ratios S_F/S_P extrapolated to 1 mm biacetyl and 0 mm N_2 at different excitation energies.

Excitation energy (bandwidth 30 Å)	$\dfrac{Y_F}{Y_P} \approx \dfrac{S_F}{S_P} \times 100\%$ at 1 mm biacetyl
4358 (22 990 cm^{-1})	2 ± 0.5%
4530 (22 075 cm^{-1})	14 ± 2%
4540 (22 025 cm^{-1})	14 ± 2%
4575 (21 850 cm^{-1})	20 ± 3%
4600 (21 740 cm^{-1})	16 ± 3%
4670 (21 410 cm^{-1})	no fluorescence

ationless rate would then be enhanced by a factor of 25.

(ii) The increase in the effective density of states. For nonstatistical manifolds (like the ^3A_u manifold in biacetyl at excitation energies employed), the existence of the second triplet leads to an appreciable increase of the number of effectively coupled states.[12] Without the existence of the ^3B_g state only triplet states of vibrational symmetry b_g are effectively coupled to the singlet. The presence of the ^3B_g state introduces strong vibronic interactions via b_u vibrations between ^3B_g and ^3A_u; therefore these states (^3A_u states of vibrational b_u symmetry) have to be counted in the effective density of states as well. Furthermore, the $^1A_u \leftarrow \!\!\!\! \rightarrow {}^3B_g$ interaction proceeds via two a_u promoting modes, instead of only one b_g mode as in the $^1A_u \leftarrow \!\!\!\! \rightarrow {}^3A_u$ interaction, thus leading to a higher density of effectively coupled states as well.[2]

The experimental results obtained can thus quite naturally be explained by the involvement of a second triplet state. Above the energy of this state the molecule behaves like a large molecule and below this energy as a small molecule since here a simple two-level system is involved. We thus come to the conclusion that there is a vibronic ^3B_g state at about 2500 cm^{-1} above ^3A_u. This locates the origin of the $^3B_g \sim 340$ or 40 cm^{-1} (the frequencies of the two possible promoting a_u vibrations) lower. Unfortunately, however, it cannot be established whether this is the ^3B_g(I) or the ^3B_g(II) configuration.

B. Extraction of the rate constants

Since hot band excitations above T_2 [^3B_g(I) or ^3B_g(II)] affect the pressure dependence of $S \rightarrow T$ crossing at low excitation energies, we select, for our discussion of the rate constants, an energy in the center of the pressure-dependent region, in particular, where the pressure dependence is most extreme (21 850 cm^{-1}). Here we locate approximately the 0–0 transition of the first excited singlet (^1A_u). From the result at this energy we can approximately determine the radiationless rate constants of the ^1A_u state at low excitation energy (0–0).

From the facts that the total light output (fluorescence and phosphorescence) increases with increasing pressure and that this increase is due to an increase of the phosphorescence (Tables I and II) we can immediately conclude that molecules, which at low pressures found their way radiationlessly to the ground state ($S_1 \rightarrow S_0$, internal conversion), are brought to phosphorescence at higher pressures, i.e., $S_1 \rightarrow S_0$ and $S_1 \rightarrow T$ are competitive processes (assuming, of course, that $T \rightarrow S_0$ is pressure independent, which is equal to saying that vibrational

relaxation in the triplet is faster than the phosphorescence lifetime which in its turn is justified by the observation that the phosphorescence spectrum does not depend on the excitation wavelength and pressure.) The fluorescence and phosphorescence yields are then given by the branching ratios,

$$Y_F = K_F/(K_F + K_{S \rightarrow S_0} + K_{S \rightarrow T}) , \qquad (1)$$

$$Y_P = CY_T = C\left[K_{S \rightarrow T}/(K_F + K_{S \rightarrow S_0} + K_{S \rightarrow T})\right] , \qquad (2)$$

where $K_{S \rightarrow S_0}$ is the rate constant for process $S \rightarrow S_0$, etc., Y_T is the triplet yield, and the constant C in Eq. (1) is determined by the radiative and radiationless rate constants from triplet to ground state, which are not functions of pressure. Biacetyl has been thoroughly studied at 4358 Å (22 990 cm^{-1}), and we assume that the rate constants at high pressure and at an energy of 21 850 cm^{-1} do not differ much from those at 22 990 cm^{-1}. This can be made plausible by noting that at any wavelength and high pressure, the molecule is "statistical" as at 22 990 cm^{-1} at all pressures. We then have at high pressure: $k_F \approx 10^5$ sec^{-1}[14]; $Y_T \approx 1$[14] and $C \approx 0.14$.[15] This means that at high pressure $K_{S \rightarrow T} \gg K_{S \rightarrow S_0}$, K_F. In order to then explain a decrease of Y_P with a factor of about 3 (Table I) in going from the high- to the low-pressure limit we must conclude that $K_{S \rightarrow S_0} \approx K_{S \rightarrow T}$ in the low-pressure limit.

From Eq. (2) and Table II it follows that:

$$Y_F/Y_P = (1/0.14)(K_F/K_{S \rightarrow T}) \approx 0.2 \text{ at } 1.0 \text{ mm} ,$$

with $k_F \approx 10^5$ sec^{-1} this leads to

$$k_{S \rightarrow T} \approx 3 \times 10^{+6} \text{sec}^{-1}$$

and

$$k_{S \rightarrow S_0} \approx 6 \times 10^{+6} \text{sec}^{-1} \text{ at } 1.0 \text{ mm pressure.}$$

Calculations[12] show that at 21 850 cm^{-1} (ΔE above 0–0 of $^3A_u \approx 1900$ cm^{-1}) the effective density of states $\rho_T \approx 10$–50 cm, i.e., the triplet manifold of vibronic states certainly cannot be considered as a quasicontinuum and thus the Fermi golden rule[16] is not expected to be valid. It has therefore no physical meaning to define an average interaction matrix element for all states. Experimentally this is clearly demonstrated by the structure in the phosphorescence excitation spectrum at low pressures, where vibrational relaxation in the singlet is slower than the electronic relaxation rate. Apparently, the triplet manifold provides a nonuniform density of effectively coupled states giving rise to a dependence of the recurrence time on the excitation energy. This structure is exactly what should be expected for small-molecule behavior, since the radiationless rate (i.e., the time evolution) depends critically on the recurrence time $t = \hbar \rho$, i.e., the time in which the oscillations between the zero-order states are damped by energy transfer. At high-

er pressures the structure disappears as expected since the vibrational relaxation rate in the triplet manifold increases and thus previously noneffectively coupled states contribute to the recurrence time, which becomes very long and structureless.

For the $S \rightarrow S_0$ radiationless process the situation is totally different. The effective density of S_0 vibronic states is very high (10^{11}–10^{12}/cm^{-1}). This means that the intramolecular recurrence time is very long and the molecule should with respect to internal conversion be considered as statistical, justifying our earlier assumption that $k_{S \rightarrow S_0}$ is pressure independent.

Application of the Fermi golden rule $k = 2\pi/\hbar \rho V^2$ gives $\langle V \rangle \approx 10^{-8}$–$10^{-9}$ cm^{-1} and $\rho(V) \gg 1$. The small magnitude of the average matrix element ($\langle V \rangle$) is, of course, a consequence of the very small Franck–Condon factor for this large energy gap. This discussion demonstrates the fact that the same molecule can behave as a small or a large molecule depending on the process under consideration.

C. Structure in the excitation spectrum

At sufficiently low pressures where vibrational relaxation in the singlet can be neglected, the structure in the phosphorescence excitation spectrum must have a connection with an energy dependence of the effective density of triplet states. The coupling between ^1A_u and ^3A_u proceeds via $\pi\pi^*$ states. Therefore, the over-all symmetry of the quantum additions in the triplet must then be b_g.[2] Since the optical modes in ^1A_u can only be of a_g over-all symmetry, this argument does not change for the higher vibrational quantum excitations in ^1A_u.

Now states with b_g over-all symmetry in the triplet manifold which can reach resonance will interact strongly with the singlet level. There is, however, no single b_g excitation in the triplet of sufficient energy to reach resonance, but double, triple, and quadruple combinations of b_g and a_g modes are frequent. The coupling via b_g modes will thus be moderated by the a_g overlap factors for combination interactions (even additions of non-totally symmetric modes can be neglected since in first order they do not contribute substantially in the Franck–Condon factor[17]). One may compare this with optical transitions: In radiationless transitions the b_g-promoting mode plays the same role as the electric dipole moment (er) in optical transitions. If an optical transition is symmetry allowed then in first order only a_g modes or combinations of a_g modes will appear in the Franck–Condon factor. One may say that a radiationless transition is just an optical transition but with $\Delta E \rightarrow 0$ (ΔE is the energy separation between the lower and higher

electronic state). A simulation of the excitation spectrum can thus be achieved by examining all $b_g + n a_g$ combinations which can reach resonance (symmetry coupled resonance states). By proceeding in this way and using the b_g skeletal bending promoting mode of 530 cm^{-1} and all known a_g frequencies (some frequencies have to be estimated from known ground state frequencies) it appears[12] that there is a qualitative agreement between the "holes" and "condensations" in the density of SCR states and minima and maxima, respectively, in the excitation spectrum, if one assumes approximately the same coupling matrix elements for all SCR states. To make the description quantitatively correct, however, we would have to calculate all Franck–Condon factors. These factors depend strongly on parameters like potential surface shifts, anharmonicities, etc., which are unknown for biacetyl. From the qualitative analysis it also appears that the SCR states in deuterobiacetyl are spread more regularly in energy, as expected since the frequencies in the deutercompounds are generally smaller. This leads to a more diffuse excitation spectrum (Fig. 3).

V. CONCLUSIONS

On the basis of the behavior of the radiationless $S \rightarrow T$ relaxation, we come to the conclusion that a second triplet is involved at excitation energies $\approx 22\,500$ cm^{-1}. The location of this triplet explains the theoretically unexpected large-molecule behavior at energies $> 22\,500$ cm^{-1}. The expected small-molecule behavior at energies $< 22\,500$ cm^{-1} is not only concluded from the pressure-dependent fluorescence and phosphorescence yields, but also from the structured phosphorescence yield as a function of the excitation energy, which should have a connection with an energy dependence of the effectively coupled triplet vibronic levels. This effect must be seen as a characteristic of small-molecule behavior as well, since it is not expected for large molecules where the dissipative manifold can be considered as a *uniform* quasicontinuum.[13]

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