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Energy Decay Characteristics of Benzophenone

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We have studied the energy-resolved decay of benzophenone in the gas phase at various pressures. In the "isolated-molecule" case benzophenone is shown to exhibit the characteristics of strong coupling between the S_1 and T_1 vibronic levels. A small contribution from weakly coupled vibrational levels may also be present and is discussed in the context of a weak coupling model.

INTRODUCTION

We have measured the time- and energy-resolved luminescence of benzophenone at low pressures, following absorption to the first excited singlet state, S_1. Whereas only phosphorescence from the lowest excited triplet state, T_1, is observed in a condensed phase,[1] it should be possible to observe efficient emission directly from the S_1 state of the isolated molecule, as the S_1–T_1 electronic energy gap is small (i.e., ~2000 cm^{-1}). An excited electronic zero-order state s of a large molecule, which is separated by a small electronic gap from a lower electronic configuration, will be strongly coupled to a sparse manifold, $\{l\}$, of zero-order states corresponding to a subset of the vibronic levels of the lower electronic state and is expected to exhibit the following decay characteristics[2]:

(a) Lengthening of the radiative decay time relative to the reciprocal radiative width of the zero-order excited state s as estimated from the integrated oscillator strength.

(b) The strong interstate coupling does not provide a pathway for electronic relaxation in the "isolated" molecule.

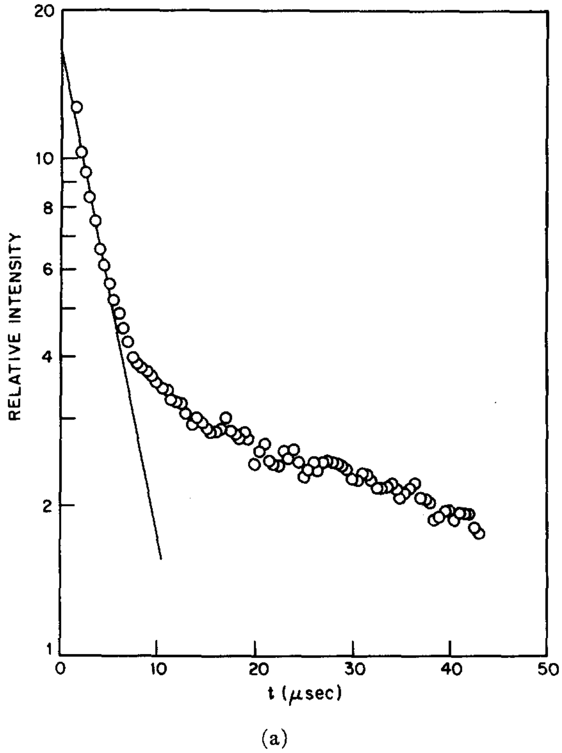
(c) $s \rightarrow \{l\}$ electronic relaxation can occur only provided that the molecule is externally perturbed by collisions which provide a broadening mechanism of the $\{l\}$ levels due to vibrational relaxation.

Simultaneously with the occurrence of the strong coupling, the s state will be weakly coupled with a relatively dense manifold $\{l'\}$ of vibronic levels corresponding to the lower electronic configuration. This weak coupling will exhibit the following effects[2]:

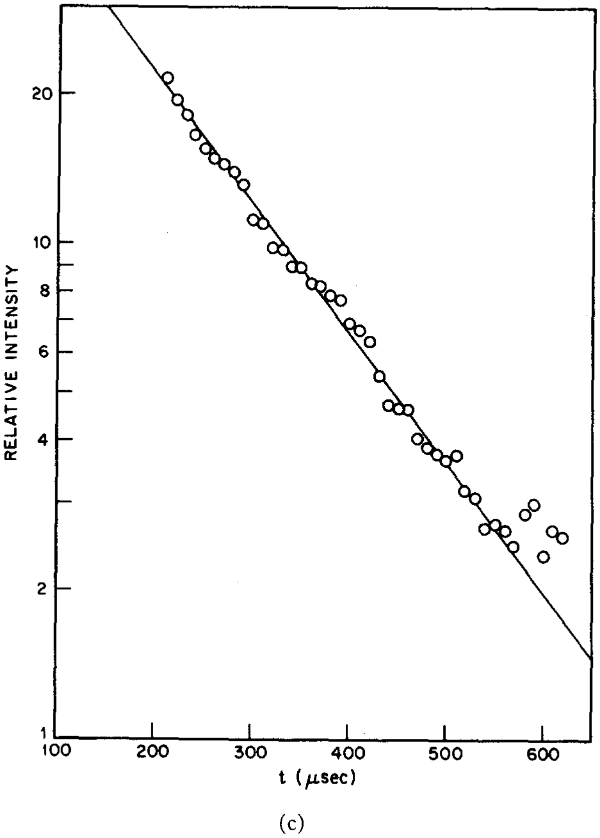
(d) An additional radiative decay component may be observed, being characterized by the radiative widths of the $\{l'\}$ states. Thus effects (a) and (d) will result in a nonexponential decay of the isolated molecule.

(e) If the weakly coupled manifold $\{l'\}$ is sufficiently dense, it may provide a dissipative statistical decay channel, resulting in a (relatively inefficient) pathway for electronic relaxation in the isolated molecule.

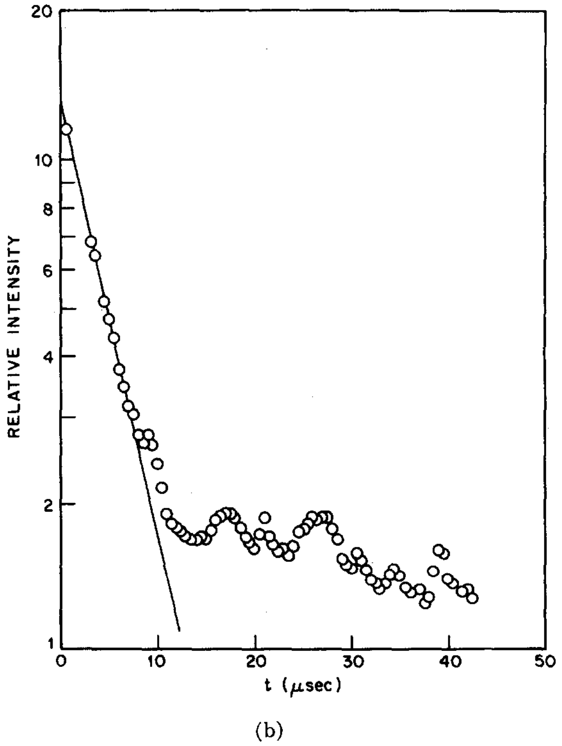
The lowest excited singlet state of the benzophenone molecule provides a good model system for the understanding of the consequences of intermediate level structure in excited electronic states of large molecules. In the present work we shall apply the results of a previous theoretical study[2] in an attempt to elucidate the importance of the (radiative and nonradiative) level widths, the magnitude of interstate coupling terms, and the densities of strongly and weakly coupled states, and to establish how these molecular parameters



(a)



(c)



(b)

FIG. 1. Typical time-resolved emission of benzophenone. (a) Intensity-vs-time plot depicting a nonexponential curve of two lifetimes at 4400 Å and 60°C. (b) Nonexponential lifetime curve at 4600 Å and 60°C. The oscillatory behavior may be indicative of molecular interference. (c) Typical long lifetime decay of benzophenone at 4400 Å and 25°C, taken with larger detector time constant and longer time scale than used for (a) and (b). The short decays of (a) and (b) are off scale in this plot.

determine the decay characteristics of an excited state which corresponds to a " dense intermediate case."

EXPERIMENTAL

Samples of benzophenone were placed into the sidearm of a Pyrex cell which was then evacuated to $\sim5\times10^{-7}$ torr and sealed off. Zone-refined benzophenone (James Hinton Company, stated purity 99.99%) was used without further purification with the exception of pumping on the cell and sample for several hours prior to sealing it off. Excitation of the samples in the spectral region about 2800 cm^{-1} above the 0–0 band of the first excited singlet was provided by a pulse of 3472-Å light from the second harmonic of a ruby laser. The laser was either *Q*-switched to obtain a 20-nsec pulse or was mode-locked to obtain a train of ~6-psec pulses with ~6-nsec separation.[3] The time-resolved luminescence was monitored with a Bausch & Lomb monochromator (dispersion 75 Å/mm) and an Amperex 56 TUVP photomultiplier, the output being displayed and photographed on Tektronix 519 or 555 oscilloscopes.

For most measurements the Pyrex cell was maintained at 100°C, while the sidearm containing solid or liquid benzophenone was thermostated from temperatures near liquid nitrogen (LN_2) up to ~80°C. The benzophenone pressure in the cell was thus controlled by the temperature of the sidearm. For measurements requiring sidearm temperatures above 80°C, the cell temperature was increased so that at least a 20°C temperature differential was maintained between the cell and sidearm. This ensured that no benzophenone condensed on walls or windows of the cell. LN_2 temperatures were used on the sidearm to freeze out the sample for background determinations, while temperatures in the region 10–150°C provided benzophenone pressures from 10^{-4} to 7 torr.[4]

The data were recorded on Polaroid film and then digitized for analysis either by hand or with a unique new photograph reader[5] easily constructed from a multichannel analyzer and other equipment normally found in a spectroscopic laboratory. The number of photographs for each experimental point varied from 5 to 50 depending upon the signal to noise (S/N) ratio. Two essentially distinct procedures were followed for data processing. In the case of intense emission the photographs were read as analog (amplitude vs time). When the pressure was low, however, the resulting weak signals were read by a photon-counting procedure (number of photons vs time interval). This method will be fully described in forthcoming papers.[6] Final values obtained for lifetimes and relative intensities are estimated to be accurate to ~20%, with the uncertainties in pressures being ~30%.

RESULTS

The time-resolved luminescence resulting from excitation of the singlet state of benzophenone at pressures $\lesssim1$ torr exhibited a nonexponential decay. Three typical decay curves measured at 60°C ($\sim6\times10^{-2}$ torr) are shown in Fig. 1. Figures 1(a) and 1(b) each show a short-lived component ($\tau=10$ μsec) and the beginning of a longer-term component. Measurements for longer time scales such as in Fig. 1(c) were made separately in order to determine the lifetime of this slower decay more accurately than can be accomplished from Figs. 1(a) and 1(b). The oscillations in the decay of Fig. 1(b) were apparent at several wavelengths and pressures, and it is possible that they are due to quantum interference as discussed below and in a forthcoming paper.

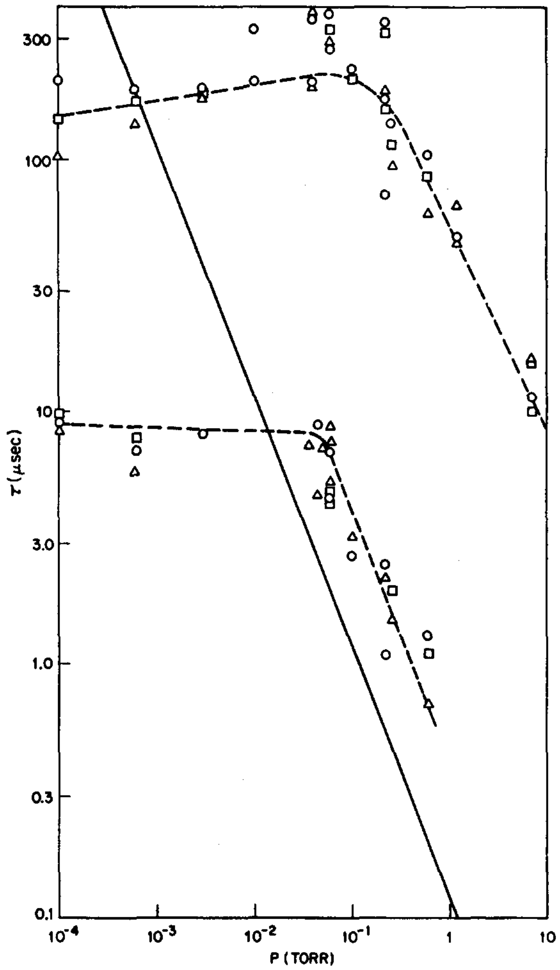


FIG. 2. Lifetime vs pressure of benzophenone vapor at 3900 Å, △; 4400 Å, □; and 5000 Å, ○. The upper dotted curve is the long lifetime (triplet) and the lower dotted curve is the short lifetime (singlet). The solid line is the gas-kinetic collisions time τ_c calculated for a molecular diameter of 5.75 Å.

Although the lifetimes are generally scattered within a factor of 2 (it should be noted that such scatter is typical for experiments of this type[7]) and many of the plots of log*I* vs *t* show up to three linear regions, the observed lifetimes break into two distinct categories at low pressure; $\tau_{1/e}\approx10$ μsec and $\tau_{1/e}\approx200$ μsec. The ob-

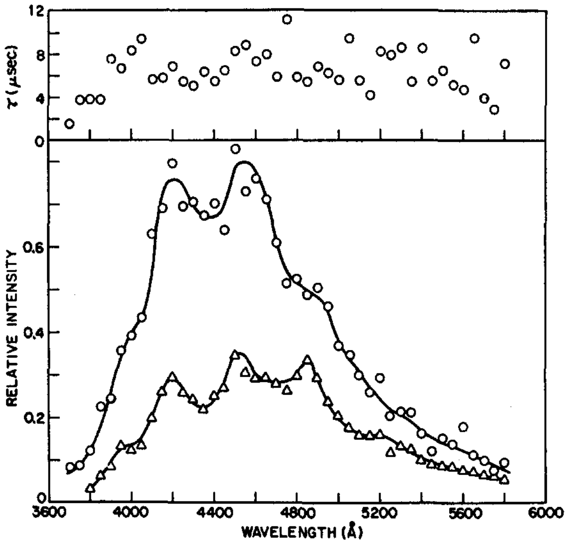


FIG. 3. Energy resolved emission of benzophenone at 60°C. Lower panel: ○, relative integrated intensity of short-lived decay component I_S; △, relative integrated intensity of long-lived component I_T. The scales for I_S and I_T are the same, so that direct comparison of the two curves may be made. Upper panel: lifetime vs wavelength for the short-lived decay component.

served lifetimes as a function of pressure are shown in Fig. 2 for three different wavelengths of emission. For reference, the pressure dependence of the gas-kinetic collision probability $Z=9.3\times10^6$ sec$^{-1}\cdot$torr^{-1} is also plotted in Fig. 2 for a molecule with a molecular diameter of 5.75 Å (obtained from the van der Waals constant for φ_2CH_2). By comparison it is seen that deactivation of the short-lived emission component by a benzophenone molecule in S_0 requires ~1–10 gas-kinetic collisions while the long-lived emission requires ~100–1000 collisions.

The "isolated"-molecule case can be realized when the time between collisions, sufficiently strong to perturb or deactivate the benzophenone molecule, is long compared with the lifetime τ_I in the isolated molecule decay, or $\tau_c/P_I \gg \tau_I$, where $\tau_c=Z^{-1}$ is the time between gas-kinetic collisions, and P_I is the probability of deactivating the excited state. Thus, up to pressures of 10^{-3} torr the collision time $\tau_c>10^{-4}$ sec is long relative to the experimentally observed short decay component which can then be considered as originating from the isolated molecule. On the other hand the isolated-molecule limit cannot be achieved with respect to the long decay component (i.e., for $\tau_I \geq 50$ μsec). Because the gas-kinetic mean free path becomes large compared to the fluorescence cell radius of 1 cm, no significance is attached to the value measured for the lifetime of the emission we attribute to phosphorescence, other than $\tau_T \geq 200$ μsec. Since an excited molecule would reach the wall after an average of ~50 μsec, this lifetime allows several collisions with the wall. The apparent small increase in lifetime with increasing pressure (see Fig. 2) for pressures up to ~10^{-2} torr, may reflect a lower quenching efficiency by collisions with ground-state benzophenone molecules than by collisions with the wall. If this long-lived emission is from the triplet, then we might expect that the radiative lifetime would be approximately that measured in glass solution or $\tau_T \approx 10$ msec.[8]

As will be discussed in the treatment of models for the radiative decay, it is assumed that the intensity, I_S, for the short emission comes mainly from a small number of mixed states which originate from strong S_1+T_1 coupling, while the intensity of the long-lived emission, I_T, is related to the spin-forbidden transitions between vibronic levels of the triplet T_1 manifold and the ground state. Following this premise, the spectral distribution of the relative intensities of emission I_S and I_T are plotted in Fig. 3 for a pressure of ~6×10^{-2} torr. The values of I_S and I_T were obtained by extrapolating the linear portion of a decay curve such as those shown in Fig. 1 to $t=0$. The intercept, multiplied by the lifetime obtained from the slope, provides the integrated intensity I_S or I_T at that wavelength, assuming that the emission in each component does in fact start at $t=0$. Errors in I_S and I_T were insensitive to errors in slope or intercept, since the two quantities are inversely related. As can be seen from Fig. 3, the emission spectra appear to be similar for I_S and I_T, both spectra span the same spectral region and are characterized by a vibrational spacing of ~1800 cm^{-1}, corresponding to the C–O stretching. It should be noted that the intensity distribution is different for the two spectra. It should be also noted that I_T appears very much like the phosphorescence $T_1 \rightarrow S_0$ observed from the lowest vibrational level of T_1 in liquid and glass solutions of benzophenone and is even more similar to the emission previously reported as delayed fluorescence for benzophenone in the gas phase at higher pressures.[9]

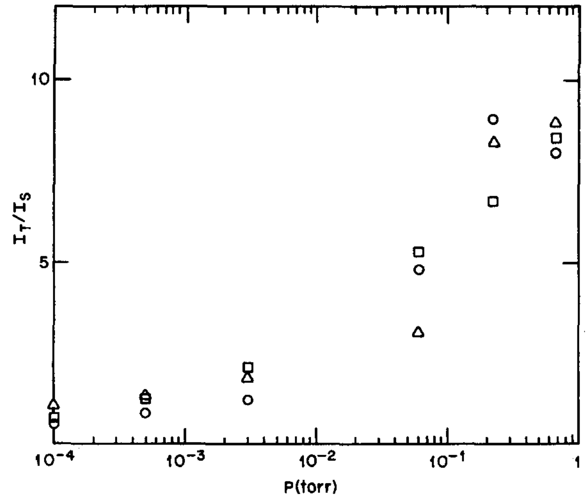


FIG. 4. Ratio I_T/I_S of triplet to singlet integrated emission intensities vs pressure at △, 3900 Å; □, 4400 Å; and ○, 5000 Å.

The structure of the emission spectrum shows some sharper bands at higher pressures in comparison with the low-pressure collision-free molecule. In the frame of the "small-molecule" model this would indicate that the smooth spectrum involves the singlet state while the structured one is due to phosphorescence originating from vibrationally relaxed triplet levels as previously shown to be the case for SO_2 and other small molecules.[7]

Although the structure appears the same for both I_S and I_T, their relative intensities appear to depend both on wavelength and on pressure. The ratio I_T/I_S as a function of pressure is plotted in Fig. 4 for wavelengths 3900, 4400, and 5000 Å. At the lowest pressure $p=10^{-4}$ torr employed in these experiments, this ratio approaches a value of $I_T/I_S \approx 0.2$–0.3, indicating that the long time emission component is exhibited also in the absence of collisional deactivation. The increase of the ratio I_T/I_S with increasing pressure (in the range $P \gtrsim 10^{-2}$ torr) suggests that the triplet levels are populated by a collisional mechanism.

We have some experimental data which indicate that the quantum yield of the triplet emission I_T is practically constant up to $p\approx 0.1$ torr and decreases with increasing pressure, at a slower rate than the singlet emission I_S decreases. Thus the predominant collisional quenching mechanism involves externally induced relaxation of the states which contain an appreciable admixture of the singlet level.

These results are discussed further below and compared to the predictions of some recently constructed[2,7] models for the energy decay of large molecules. We will see that the results can best be interpreted by a model in which there is strong coupling between the S_1 level originally populated and several levels in the T_1 state and where simultaneously, the S_1 level is weakly coupled to a large number of levels in the T_1 manifold. Before we make this comparison, however, we will qualitatively discuss some models for three different coupling cases that might be important among vibronic levels of excited electronic states.

MODELS FOR RADIATIVE DECAY

The radiative decay of excited electronic states in large molecules has received considerable theoretical attention in recent years.[2,10,11] In particular, some general criteria have been given for predicting the characteristics of the radiative decay from levels corresponding to the dense intermediate-level-spacings situation. These criteria have been applied with reasonable success to the luminescence of 3,4-benzpyrene[12] and of naphthalene[13] excited to their second singlet S_2. In those cases the coupling takes place between lower vibronic levels in S_2 and a subset of the upper levels of the S_1 state. In view of the strong coupling between the S_1 state and some of the upper levels of the T_1 state in benzophenone[14–16] we might expect the same treatment of coupling mechanisms and radiative decay to apply for the present case, when the isolated molecule is excited to lower vibronic levels of S_1.

We qualitatively review here the model for this treatment, apply it to benzophenone, and extend the isolated-molecule model to higher pressures, which would enhance the model further and bring it closer to real life situations. These models are classified according to relative magnitudes of the coupling term between a single pair of S_1 and T_1 levels, v_{ST}, and to the energy separation and total widths γ_S and γ_T of the individual levels. The width of a level, i, is made up of two components,[17]

$$\gamma_i=\Gamma_i+\Delta_i, \tag{1}$$

with Γ_i being the radiative width and Δ_i being the nonradiative contribution due to radiationless transitions to dissipative continua such as the ground state S_0. We assume for simplicity that Δ_i due to the decay to the ground state is negligible although it need not be so. The magnitude of this width can be estimated from measurements of quantum yield of total luminescence.

No Intramolecular Coupling

We consider first the simplest model for the radiative decay of an excited electronic state, namely, one in which there is neither intramolecular coupling between the S_1 state being excited and the upper vibrational levels of the T_1 state, nor with very high vibrational levels of S_0. For the isolated molecule we would then expect to observe resonance fluorescence to S_0 with a quantum yield of one and characterized by a single radiative lifetime essentially equal to that calculated from the integrated absorption oscillator strength. Franck–Condon factors would limit the emission to lie close to the energy of the exciting radiation. A possible description for the magnitude of the coupling term in this case would be

$$|v_{ST}| \lll \Gamma_S \tag{2}$$

for all T levels. This indicates that the excited S_1 level would undergo complete radiative decay before significant transitions to T levels could take place.

Strong Coupling Model

The next model we consider is one in which the levels in the S_1 state populated directly by photon absorption are strongly coupled to a sparse set of upper vibrational levels in the T_1 manifold. If the coupling is sufficiently strong then the coupled levels in the S_1 and T_1 manifolds are completely scrambled. The situation can be represented by

$$|v_{ST}| \gg |E_T - E_{T_1}| \tag{3}$$

for all T, T_1, in which T and T_1 are two adjacent strongly coupled levels in the T manifold.

The strong coupling of levels has the effect of causing the mixed state composed of coupled S_1 and T_1 levels to decay with a single lifetime. Since only the S_1 levels contributing to this mixed state carry an appreciable oscillator strength, the radiative decay will look primarily like that of the S_1, but "diluted" by the T_1 levels that are mixed in. The lifetimes will be increased in proportion to the amount of dilution by the states without oscillator strength. We are considering excitation of the singlet state near its origin ~ 2800 cm^{-1} above the 0–0 band. The origin of the T_1 state is located about 2000–3000 cm^{-1} below the origin S_1, thus the total density of states in the region of T_1 where S_1 is being pumped will be $\sim 10^5$ cm. As was argued by Nitzan *et al.*[2] the number of the strongly coupled levels in the triplet manifold should be greatly restricted by symmetry considerations and Franck–Condon factors, so that the number of levels strongly coupled to S_1 may be low. If we call this number n and the linewidths in the isolated molecules for uncoupled levels in each manifold, γ_s and γ_t, then the observed lifetime τ_I for the single exponential decay in the strong coupling model of the isolated molecule should be

$$\tau_I = \hbar(\gamma_S/n + \langle\gamma_T\rangle)^{-1}, \tag{4}$$

where $\hbar = 1$ for all cases subsequently discussed. Maintaining our approximation that Δ, the intramolecular relaxation width of S_1 and T_1 to S_0, is negligible for the isolated molecule, the total quantum yield of the radiative decay from this level should be unity. However, each of the manifolds still couples to its own radiation field, hence emission in separate spectral regions should be observed. The ratio R of the quantum yields in the S_1 and T_1 spectral regions, assuming a total quantum yield of unity, should be determined by the ratio of their "effective" widths or

$$R = \Gamma_S / n\langle\Gamma_T\rangle \tag{5}$$

in which $\langle\Gamma_T\rangle$ is the average radiative width of the coupled levels in the T manifold. The expressions[2] for the time-dependent intensities $I_S(t)$ and $I_T(t)$ of the radiative decay in the S_1 and T_1 regions are

$$I_S(t) = (\Gamma_S/n)[\exp(-t/\tau_I) + \Omega_S(t)], \tag{6a}$$

$$I_T(t) = \Gamma_T[\exp(-t/\tau_I) + \Omega_T(t)]. \tag{6b}$$

The mixed-state lifetime τ_I is given by Eq. (4), while the last terms on the right $\Omega_S(t)$ and $\Omega_T(t)$ are "interference terms" which will be discussed below.

Weak Coupling Model

We will now consider what the characteristics should be for luminescence from states composed of weakly coupled levels of the S_1 and T_1 states.

A qualitative picture for processes taking place starts with the system excited to a set of vibronic levels in the S_1 state. Considering again an isolated-molecule case and assuming that intramolecular internal conversion to S_0 is small, the S_1 state then decays radiatively with lifetime $\gamma_I^{-1} \approx \gamma_S^{-1}$.

The degree of coupling between the S_1 and T_1 levels is defined[2] by the average coupling constant $\langle v_{ST}\rangle$ which satisfies the following conditions:

$$\langle v_{ST}\rangle \ll E_S - E_T, \tag{7a}$$

$$\langle v_{ST}\rangle \ll |\gamma_S - \gamma_T|, \tag{7b}$$

where E_S and E_T are the energies of the singlet (E_S) and triplet (E_T) levels and γ_S, γ_T are their respective total widths in the absence of S_1–T_1 coupling. When Eqs. (7) are satisfied then conventional perturbation theory can be used to obtain the resulting lifetimes for S_1 and T_1 states.

In the case of slightly perturbed singlet S_1 and triplet levels T_1, the lifetimes τ_S' and τ_T' for these states are expressed by[2]

$$\tau_S' = (\gamma_S')^{-1} = [\gamma_S + \bar{n}v(\gamma_T - \gamma_S)]^{-1}, \tag{8a}$$

$$\tau_T' = (\gamma_T')^{-1} = [\gamma_T + v(\gamma_S - \gamma_T)]^{-1}, \tag{8b}$$

where $\bar{n}$ is the number of T levels to which the S level is weakly coupled, and v is the second-order term,

$$v = |v_{ST}|^2 / [(E_S - E_T)^2 + (\gamma_S - \gamma_T)^2] \ll 1. \tag{9}$$

The energy-resolved decay lifetimes of the singlet or triplet spectral regions will *not* exhibit a purely exponential shape with a lifetime corresponding to either the singlet or triplet state. Instead one should observe emission characterized by a nonexponential decay whose intensity vs time will be a function represented by

$$I_S(t) = \Gamma_S\{\exp(-\gamma_S t) + \bar{n}v^2 \exp(-\gamma_T t) + 2\bar{n}v \exp[-\tfrac{1}{2}(\gamma_S + \gamma_T)t] \cos[\Delta E(1+2v)t]\}, \tag{10a}$$

$$I_T(t) = \bar{n}\Gamma_T v\{\exp(-\gamma_S t) + \exp(-\gamma_T t) - 2\exp[-\tfrac{1}{2}(\gamma_S + \gamma_T)t] \cos[\Delta E(1+2v)t]\}, \tag{10b}$$

with $\Delta E = \langle E_S - E_T\rangle$, the average separation between the S level and the weakly coupled T levels. The last term on the right in both Eqs. (10a) and (10b) is an interference term which may give rise to "beats" in the decay. The feasibility of observing beats will be discussed briefly in a later section of this paper and fully in a forthcoming article.[18]

Ignoring these terms for the time being, the remaining two terms in each equation give simply a nonexponential decay with short life τ_S' and a long component τ_T'. This result is in contrast to the single exponential decay obtained for the strong coupling model presented above. Thus by monitoring the time dependence of the decay of emission of an isolated-molecule system, it is possible within the framework of this model to determine the extent of coupling directly.

It should be noted that although such assignments are necessarily model dependent, they do not entirely depend on all of the assumptions of the model on an all-or-nothing basis. We have assumed, for example, that emission from S and T manifolds occurs in separate spectral regions. This need not be true, as the sum of Eqs. (10a) and (10b) is still nonexponential, with the same two components distinguishing the weak coupling case from the single-component decays of the strong coupling and complete absence of coupling cases. In turn, the increased lifetime for the strong coupling situation, over that calculated from the integrated oscillator strength, is clearly distinguishable from the lifetime of the no coupling case, for which the measured value should be close to the calculated value. The assumption we have made about negligible radiationless transition to the ground state can be readily ascertained by the quantum yield of luminescence.

Quantum Beats

The models for the radiative decay of coupled electronic states are an exact analog to the coupled harmonic-oscillator problem in mechanics, with decay corresponding to damping. As in the harmonic-oscillator problem, if just one of the oscillators of a coupled pair is excited initially, the excitation will move from one oscillator to the other and back again with a frequency which depends on the coupling constant and the difference in frequency of the uncoupled oscillators. This periodic amplitude change is represented by the last term in Eqs. (6) and (10) for strong and weak coupling cases, respectively.

Whether or not these "beats" will be observable in the radiative decay of the excited electronic state is both a theoretical and an experimental problem. That interference effects should be present on some level seems unmistakable. That they will be sufficiently large compared to the purely exponential portion of the emission and amenable to experimental observation, depends upon the molecular system studied, the coupling between the levels, and density of states. For example, if we consider the weak coupling case described by Eq. (10), we see that in this extension of a two-level coupled system to n levels, it was assumed that all of the separations between the S level and the n coupled levels in the T manifold are essentially the same and equal to the average value ΔE. If the spread of this average for many coupled levels was $\sim 2\Delta E$, which is not at all unlikely in many molecular systems, and the number of coupled levels is large, then the beats would be expected to damp out after a single oscillation, making their observation difficult. Further complications might be expected if a large number (~ 100) of levels in the S_1 state which are optically accessible due to sequence broadening fall within the bandwidth of the laser.

The optimum situation for observation of beats should occur when the period of oscillation is on the same time scale as the damping or lifetime. If the period is considerably longer than the lifetime, then the signal will be essentially gone before a single oscillation can be observed. When the period is considerably shorter, then the total light emission during the time scale of a few oscillations is small, leading to reduced S/N. The second of these situations is, of course, preferable to the first, because one can fit a "locally noisy" set of data to a long train of oscillations and still obtain a relatively high over-all S/N.

In spite of the experimental difficulties and the complications introduced when n, the number of coupled levels, becomes large, we would expect that quantum beats should be observable in many isolated-molecular systems. Beats have been observed in atomic systems for some time,[19,20] but have not yet been observed in molecules, with the possible exception of 3,4-benzpyrene.[12] The most likely candidate would be the small molecules with accidental near degeneracies between two or very few levels, so that n is small, yet ΔE is also small. Such systems would still, however, lack generality and would not be as interesting as would be the case if a large number of molecular systems exhibited "small molecule" properties, as proposed recently.[2] In those systems considered, the band gap is sufficiently small between two separate electronic states (S_2–S_1, or as we consider here, S_1–T_1) that n, the number of strongly coupled levels in the lower state, is sufficiently small for the beats not to "wash out," as described above; yet the density of levels is sufficiently high that there are always coupled levels with ΔE small. Such systems may, in fact, be encountered in real life.

Benzophenone Model

We shall now turn to a model which will attempt to reproduce a real life situation and which will hopefully account for the features of the radiative decay of the lowest excited singlet state of the benzophenone molecule. We shall consider the radiative decay of the isolated molecule and then attempt to generalize the treatment in order to account for collisional quenching effects.

Focusing attention on the model system presented in Fig. 5, we notice that an optically accessible zero-order singlet state, S, will not couple with all the states in the triplet manifold (which are characterized by a total state density $\sim 10^5$ cm) with the same efficiency. The majority of these triplet levels will be characterized by a wrong symmetry or by unfavorable Franck–Condon factors which will prevent their efficient coupling to S. There will be a small number n of triplet levels, which we denote by T, which will be strongly coupled to S. This strong S–T coupling does not result in intramolecular relaxation in the isolated molecule. On the other hand, when the benzophenone molecule is embedded in solution,[14] efficient intersystem crossing will occur as the strongly coupled T levels are now appreciably broadened due to vibrational relaxation. The approximate value of $v_{ST} \approx 1$ cm^{-1} derived from previous experiments[14] satisfies the criteria of Eq. (3) for strong coupling. If only this strong intramolecular coupling would prevail in the isolated molecule, we would expect emission characterized by the radiative decay time [see Eq. (6)] $[(\Gamma_S/n)+\Gamma_T]^{-1}$ provided that nonradiative decay to the ground state is neglected

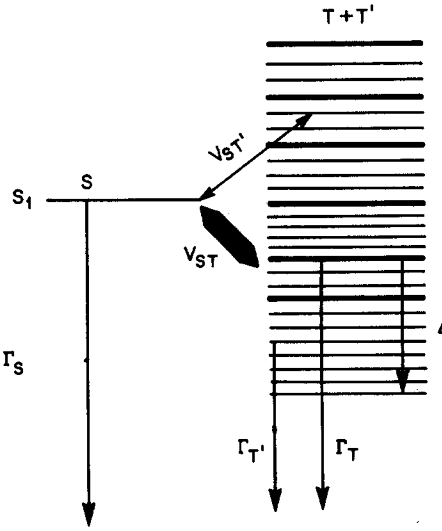


FIG. 5. Schematic energy-level diagram of the zero-order state of benzophenone depicting the coupling models considered in the text. The zero-order S state exhibiting both strong v_{ST} and weak $V_{ST'}$ coupling. The radiative widths of the zero-order states are Γ_S and $\Gamma_T\approx\Gamma_{T'}$ ($\Gamma_S\gg\Gamma_T$). The pressure-induced vibrational relaxation width Δ_T^v results in the reduction of the short-lived decay component at higher pressures.

and radiative interference effects are disregarded. Thus the effects of strong coupling with a sparse manifold will exhibit the effect of the "dilution" of the width of the zero-order state Γ_S among a number of molecular eigenstates resulting in the lengthening of the decay time.

As a rough estimate we utilize the experimental value of the short decay time $\tau_I\approx10$ μsec, the value of $\Gamma_S^{-1}\approx1$ μsec calculated from the integrated oscillator strength,[16] and the value of $\hbar\Gamma_T^{-1}\approx5\times10^3$ μsec obtained from low-temperature phosphorescence studies[8,16] in a rigid glass, noticing that $\Gamma_S\gg\Gamma_T$. Making use of Eq. (4) we get $n\sim10$. This result clearly demonstrates that although the total density of levels in the triplet manifold is $\sim10^5$ cm, only a small number of levels effectively couple with S, so that the gross features of the radiative decay of the singlet state can be accounted in terms of the "small-molecule" model.

A large number of levels in the triplet manifold are weakly coupled to S. This physical situation can be adequately described by considering each of the $n+1$ levels which resulted from strong coupling being weakly coupled to a large number of $\{T'\}$ states in the triplet manifold. As already discussed above, this weak coupling will result in a long radiative component in the isolated molecule, being characterized by the radiative width $\Gamma_{T'}^{-1}\approx\Gamma_T^{-1}$. If the weakly coupled $\{T'\}$ manifold is sufficiently dense it may provide a dissipative quasicontinuum. The total density of triplet states quasidegenerate with S provides a recurrence time[17] (independent of the coupling strength) of ~10 μsec for the decay of the singlet state into this manifold. It should be also noted that radiative broadening mechanisms of the T' levels, due to the radiative decay to the ground state and to infrared emission within the T' manifold,[17,21] will bring this $\{T'\}$ quasicontinuum to the verge of the statistical limit. It should be noted however that in view of the weak S–T' coupling, this intramolecular $S\rightarrow\{T'\}$ relaxation is not expected to be very efficient. The experimental observation (see Fig. 4) that at $p\simeq10^{-4}$ torr the yield of the long decay component does not vanish and $I_T/I_S\approx0.2$–0.3, indicates the role of weak coupling in the decay of the isolated molecule.

As a further test of the validity of this physical picture we consider what happens when the pressure is increased. If absorption populates strongly mixed $S+T$ states, weakly coupled in turn to $\{T'\}$, then a subsequent collision will provide a pathway for vibrational relaxation in the triplet manifold. Thus a zero-order T level will be vibrationally deactivated to a lower T_1 state (which is not necessarily strongly coupled to the singlet manifold or even may lie below the origin of the singlet manifold.) This collisional deactivation may be qualitatively described[22] by assigning a vibrational relaxation width Δ_T^v to the states T, and it is assumed[22] that this width will be proportional to the pressure of the perturbing gas molecules, $\Delta_T^v=\Delta_T^0p$. We shall also further assume that collisions do not appreciably affect the width of the excited S state. Thus the collisionally induced relaxation of the T states will shorten the short decay time (due to the additional width Δ_T^v) and reduce its quantum yield. The vibrationally relaxed states in the triplet manifold resulting from deactivation of the strongly coupled T levels will result in a long radiative decay characteristic of the triplet state, and the yield of this decay component will increase with increasing pressure. Finally we should notice that provided that the $\{T'\}$ weakly coupled manifold is statistical, collisionally induced vibrational relaxation of the $\{T'\}$ states will not affect the decay of the states which contain an appreciable admixture of the S state. Up to pressures of 1 torr (see Figs. 2 and 4) where the lifetime and yield of the long-lived component are practically constant, we do not have to worry about the collisionally induced decay of the triplet states (apart from wall collisions which introduce a complicating experimental factor) and can assign the increase in the triplet yield to deactivation of the strongly coupled levels. At high (>1 torr) pressures the vibrational relaxation within the triplet manifold should be fast, and the emission should come from near the origin of the triplet state.

To provide a semiquantitative formulation of these ideas let us consider the decay of some of the $n+1$ molecular eigenstates $|j\rangle$ ($j=1\cdots n+1$) resulting from mixing of S and n of T levels. Each of these zero-order j states is now characterized by the total width

$$\gamma_j=(\Gamma_S/n)+\Gamma_T+\Delta_T^v \qquad (11)$$

and is weakly coupled to the $\{T'\}$ manifold by the coupling terms

$$|v_{jT'}| = |\langle j | v_{T'} \rangle| \approx (1/n^{1/2}) | v_{ST'} |, \qquad (12)$$

where V is the intramolecular (spin–orbit and adiabatic) coupling, whereupon $\langle T' | v | T \rangle = 0$. Note also that $v_{ST'} \ll v_{ST}$.

Consider now the case when the $\{T'\}$ manifold is statistical. Each of the $|j\rangle$ states will now acquire an additional width

$$\begin{aligned}\Delta_{jT'} &\approx 2\pi \, | v_{jT'} |^2 \rho_{T'} \\ &= 2\pi \, | v_{ST'} |^2 \rho_{T'}/n = \Delta_{ST'}/n,\end{aligned} \qquad (13)$$

where $\rho_{T'}$ is the density of states in the $\{T'\}$ manifold, while $\Delta_{ST'}$ is the total width of the S level due to intramolecular relaxation. As expected, this total width is distributed among the molecular eigenstates j. The states $\{T'\}$ now decay radiatively, being characterized by a radiative width $\Gamma_{T'} \approx \Gamma_T$. Thus we encounter a physical situation of consecutive decay where the $|j\rangle$ states decay nonradiatively into $\{T'\}$ which in turn decay radiatively into the ground state. Such a consecutive decay scheme has been recently considered,[23] and the results are directly applicable to the problem at hand. In the absence of interference effects between the $|j\rangle$ levels, the time-dependent intensity can be recast as a superposition of a short-time and a long-time component,

$$I(t) = I_S(t) + I_T(t), \qquad (14)$$

where

$$I_S(t) = \left(\frac{\Gamma_S}{n} + \Gamma_T\right) \exp\left[-\left(\frac{\Gamma_S + \Delta_{ST'}}{n} + \Gamma_T + \Delta_T{}^v\right) t\right] \qquad (15a)$$

and

$$I_T(t) = \frac{\Gamma_{T'}[(\Delta_{ST'}/n) + \Delta_T{}^v]}{[(\Gamma_S + \Delta_{ST'})/n] + \Delta_T{}^v} \times \left\{\exp(-\Gamma_{T'} t) - \exp\left[-\left(\frac{\Gamma_S + \Delta_{ST'}}{n} + \Gamma_T + \Delta_T{}^v\right) t\right]\right\}. \qquad (15b)$$

The quantum yield Q for emission can be represented in a similar way as a superposition from the contribution from the two components:

$$Q = Q_S + Q_T, \qquad (16)$$

where

$$Q_S = \frac{(\Gamma_S/n)}{(\Gamma_S/n) + \Gamma_T + (\Delta_{ST'}/n) + \Delta_T{}^v} \qquad (17a)$$

and

$$Q_T = \frac{(\Delta_{ST'}/n) + \Delta_T{}^v}{(\Gamma_S/n) + \Gamma_T + (\Delta_{ST'}/n) + \Delta_T{}^v}. \qquad (17b)$$

From Eqs. (14)–(17) we conclude that for the dense intermediate case the features of the radiative *decay* are as follows:

(a) The short radiative decay component is characterized by the exponential decay time,

$$\tau_1 = \{[(\Gamma_S + \Delta_{ST'})/n] + \Delta_T{}^v\}^{-1}, \qquad (18)$$

provided that $\Gamma_T \ll \Gamma_S/n$. In the isolated-molecule case, $\Delta_T{}^v = 0$ and one gets

$$\tau_1(p=0) = [(\Gamma_S + \Delta_{ST'})/n]^{-1}, \qquad (19)$$

while at higher pressures, the reciprocal decay time should increase with $\Delta_T{}^v$, i.e., linearily with pressure.

(b) The long decay [Eq. (15b)] is characterized by a consecutive decay scheme. For sufficiently long time (relative to the short decay component) the long decay will be characterized by the lifetime $\Gamma_{T'}{}^{-1} \approx \Gamma_T{}^{-1}$; according to the present model, which neglects (intramolecular or collision induced) relaxation into the ground state, this long decay time is pressure independent.

(c) The quantum yield for the short component [Eq. (17a)] in the isolated-molecule case is (assuming again that $\Gamma_T \ll \Gamma_S/n$)

$$Q_S(p \to 0) = \Gamma_S/(\Gamma_S + \Delta_{ST'}), \qquad (20a)$$

which just corresponds to a single branching ratio between radiative decay and intramolecular relaxation. Note that Eq. (17a) at finite pressures just corresponds to the classical Stern–Volmer relation, which is valid in the absence of interference.[22]

(d) The quantum yield for the long component consists of two terms [see Eqs. (17b) and (15b)]. The first term involving $\Delta_{ST'}/n$ in Eqs. (17b) and (15b) corresponds to the population of the $\{T'\}$ levels by intramolecular relaxation, while the second term, determined by $\Delta_T{}^v$, corresponds to feeding the triplet manifold by vibrational relaxation of the strongly mixed $|j\rangle$ states. In the isolated-molecule limit (where again $\Gamma_T \ll \Gamma_S/n$) we have

$$Q_T(p \to 0) = \Delta_{ST'}/(\Gamma_S + \Delta_{ST'}). \qquad (20b)$$

(e) The ratio between the yields for the short- and long-lived emissions,

$$\frac{Q_S}{Q_T} = \frac{\Gamma_S/n}{(\Delta_{ST'}/n) + \Delta_T{}^v}, \qquad (21)$$

exhibits a Stern–Volmer relation (in the absence of interference effects). In the "isolated"-molecule limit this ratio takes the form

$$(Q_S/Q_T)(p=0) = \Gamma_S/\Delta_{ST'}. \qquad (22)$$

Two additional points are worth mentioning:

(a) When the S–T' coupling is too weak to provide intramolecular relaxation (i.e., $\Gamma_S \gg \Delta_{ST'}$) Eqs. (14)–(22) are valid provided that we set $\Delta_{ST'} = 0$.

(b) The photon conservation law holds, i.e., $Q_S + Q_T = 1$.

Turning now to our experimental data for the decay of the first excited state of the benzophenone molecule in the low-pressure gas phase we note that:

(a) The finite value of $I_S/I_T \approx 5$ at $p \approx 10^{-4}$ torr indicates [see Eq. (22)] that $\Gamma_S/\Delta_{ST'} \approx 5$. This ratio may in fact be somewhat lower in view of wall collisions which may reduce the quantum yield for the triplet emission. The finite value of the I_T yield at low pressures is now adequately rationalized.

(b) Making use of the experimental short decay time we have [see Eq. (20a)]

$$[(\Gamma_S/n)+(\Delta_{ST'}/n)]^{-1}=[(\Gamma_S/n)+(\Gamma_S/5n)]^{-1} \quad (23)$$

$$=10\ \mu\text{sec},$$

and utilizing the spectroscopic value $\Gamma_S^{-1}=1\ \mu$sec we derived again the value $n \sim 10$. Note that if wall collisions reduce the observed long-component quantum yield the value of n will somewhat increase. We conclude that the major contribution for the lengthening of the decay lifetime of the short component relative to the estimates based on the integrated oscillator strength results from strong interstate coupling.

(c) The pressure dependence of the short-component decay time and its quantum yield (Figs. 2 and 4) is adequately interpreted in terms of the theoretical Stern–Volmer relations (18) and (17a).

CONCLUSIONS

The luminescent decay of the lowest singlet state of benzophenone exhibits predominantly the characteristics of strong interstate singlet–triplet coupling. A contribution from the weakly coupled levels is responsible for the long lifetimes in the isolated molecule. An adequate interpretation of collisional quenching has been also provided. It is interesting to note in this context that the ground-state benzophenone molecule may be a very efficient quencher for inducing vibrational relaxation in the electronically excited state of the same molecule by a near-resonance vibrational energy transfer. A vibrational quantum is excited in the ground electronic state of the quencher while a vibrational quantum is simultaneously annihilated in the excited electronic state of the second molecule. This "vibrational exciton" transfer mechanism will be more efficient than vibrational quenching of the excited electronic state by other foreign gases (i.e., He). At present we are studying the role of C=O infrared emission in the relaxation process of benzophenone, which was previously observed in the decay of the biacetyl molecule.[21] Another interesting problem involves the observation of quantum beats in the radiative decay.[18]

Although some of the effects reported here have been observed[12,13] for S_2–S_1 coupling in large molecules, we believe that the present system is of particular interest for exhibiting the effects of S–T coupling. The effects of strong interstate S–T coupling for the "dense intermediate case" are more dramatic than previously observed[12,13] for the intermediate S_2–S_1 coupling. In the present case, $\Gamma_S/n \gg \Gamma_T$ whereupon the radiative decay is nonexponential, while in the former case[12] $\Gamma_{S_2}/n \sim \Gamma_{S_1}$, so that a single decay time was observed. We believe that the implications of the present study are general for the elucidation of time implications of intramolecular interstate coupling in large molecules. The interstate coupling matrix elements will in no case be constant or slowly varying. In the statistical limit a "coarse-graining" procedure is justified, as is the case of nuclear reactions in the statistical nucleus. For a small energy gap in a large molecule the effects of the variation of the coupling strengths are amenable to experimental observation, similar to those encountered in the present study.

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