For **6e**·$(H_2O)_3$, no H atoms were located near the central water oxygen; H atoms in hydrogen bonds of water with ether oxygens were found on a final difference Fourier map. For **6c**·$(H_2O)_2$ and **6e**·$(H_2O)_3$, macrocyclic H atoms were put in calculated positions and treated as riding on their parent C atoms. Further details concerning the treatment of the H atoms are in the supplementary material. For **6e**·$(H_2O)_3$, two C atoms could not be refined anisotropically, due to the poor data quality. Parameters refined were the overall scale factor, an isotropic extinction parameter $g\ \{F_o = F_c/(1 + gI_c)\}$, positional and anisotropic thermal parameters for non-H atoms, and positional and isotropic thermal parameters for H atoms. Although for **6c**·$(H_2O)_2$ and **6e**·$(H_2O)_3$ the macrocyclic H atoms were not refined independently, the data-to-variable ratio was still rather low. Refinement converged with shift/error ratios less than unity. Final difference Fourier maps showed no significant features, except the peaks for **6e**·$(H_2O)_3$ near two water oxygens, which were assumed to be H atoms. All calculations were done with SDP.[37] Views of the structures, showing 50% probability thermal ellipsoids for non-H atoms and spheres of arbitrary size for H atoms, were produced with ORTEP.[38]

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Supplementary Material Available: ORTEP drawings and tables of positional and thermal parameters of all atoms, bond distances and angles, and torsion angles in the macrocycle, for the crystal structures of compounds **5a**, **6b**·Li·H_2O, **6a**·H_2O, **6c**·$(H_2O)_2$, and **6e**·$(H_2O)_3$ (23 pages). Ordering information is given on any current masthead page.

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Resolution of Benzophenone Delayed Fluorescence and Phosphorescence Spectra. Evidence of Vibrationally Unrelaxed Prompt Benzophenone Fluorescence[1]

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Abstract: Resolution of the delayed fluorescence and phosphorescence spectra of benzophenone was achieved by application of principal component analysis combined with a self-modeling technique on a set of benzophenone emission spectra from degassed carbon tetrachloride solutions in the −2.4 to 85.2 °C temperature range. The temperature dependence of the quantum yield ratio of the two emissions gives $\Delta H = 6.3 \pm 0.3$ kcal/mol which, though significantly higher than previous estimates, is in excellent agreement with the spectroscopic S_1–T_1 splitting. Calculation of $k_f = 1.1 \pm 0.1 \times 10^6$ s^{-1} for the radiative fluorescence rate constant with the Birks–Dyson equation allows estimation of $\Delta S = 0.73 \pm 1.0$ gibbs/mol for triplet $\rightleftarrows$ singlet equilibration from the intercept of the van't Hoff plot. The positive value of ΔS together with the more diffuse vibrational structure of the fluorescence spectrum relative to the phosphorescence spectrum suggest a larger geometry change for the $S_1 \rightarrow S_0$ than for the $T_1 \rightarrow S_0$ transition. Substantial differences between our measured prompt fluorescence spectrum of benzophenone and the delayed fluorescence spectrum demonstrate that the short S_1 lifetime prevents full relaxation of emitting benzophenone singlets. Differences between our prompt fluorescence spectrum and earlier time-resolved spectra are discussed.

Benzophenone is a widely used triplet energy donor and its photochemistry and photophysics have been thoroughly studied. Many years ago we demonstrated that excitation of benzophenone in CCl_4 solutions gives rise to emission which is composed mainly of delayed fluorescence (DF) and phosphorescence (P) originating from thermally equilibrated S_1 and T_1 states,[2] as reported earlier for benzophenone in the vapor phase.[3] The observation of DF in solution[4] and in rigid media[5] was confirmed shortly thereafter in other laboratories.

The scheme in Figure 1 summarizes the kinetic processes of the lowest singlet and triplet excited states of benzophenone in solution. The rate constants k_f, k_{is}, k_{-is}, k_p, and k_d represent fluorescence, intersystem crossing ($S_1 \rightarrow T_1$), back-intersystem crossing ($S_1 \leftarrow T_1$), phosphorescence, and nonradiative triplet decay, respectively. Because the S_1–T_1 energy gap is small and T_1 is relatively long-lived (~100 μs in CCl_4), the two excited states reach thermal equilibrium at moderate temperatures.[2-5] The severe overlap between DF and P spectra can also be attributed to the small S_1–T_1 energy gap. A van't Hoff plot based on the assumption that emissions at 2.56 and 2.06 μm^{-1} consisted of pure DF and P, respectively, gave $\Delta H = 4.4$ kcal/mol.[2] A slightly larger value was obtained by using a benzophenone time-resolved fluoresence spectrum to subtract the contribution of fluorescence from the total 2.06-μm^{-1} luminescence intensity.[4] Since a proper van't Hoff treatment of the temperature dependence of the luminescence spectra requires knowledge of the exact DF and P spectra, we undertook the resolution of the spectra by application of principal component analysis in combination with the self-modeling method (PCA-SM).[1] The successful resolution of the benzophenone DF and P spectra and a reinvestigation of benzophenone's prompt fluorescence (PF) are reported here.

Experimental Section

Materials. Benzophenone (Fischer, Certified Reagent) was twice recrystallized from hexane and then triply sublimed before use. Carbon

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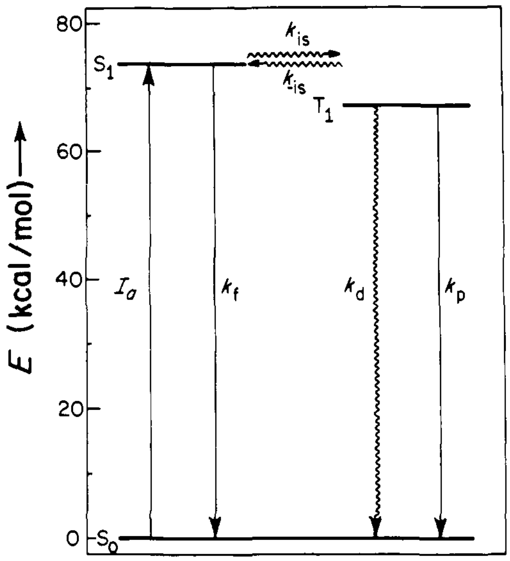

Figure 1. Benzophenone state diagram and rate constants.

tetrachloride (Mallinkrodt, SpectrAR) was distilled prior to use. For DF/P measurements benzophenone solutions 1.04×10^{-2} M in CCl_4 were deaerated by several freeze-pump-thaw cycles at ca. 1.0×10^{-5} Torr. Prompt fluorescence was measured for the same solutions but in the presence of air and 0.1 M **trans-1,3-pentadiene** (Aldrich, Reagent). *trans*-1,3-Pentadiene was filtered through a short silica column immediately prior to use.

Data Collection. All luminescence measurements were made with a Hitachi/Perkin-Elmer MPF-2A fluorescence spectrophotometer equipped with a 150-W Xe arc source and a Hamamatsu R106 photomultiplier tube. Emission intensities were recorded at each 0.5-nm interval directly on a Compupro 816/286 microcomputer equipped with an I/O Technology A/D/A converter board. The scan rate was 200 nm/min. Slit widths for DF/P measurements were set at 7.5 and 4.5 nm for excitation and emission monochromators, respectively, and for PF at 10.0 nm (excitation) and 8.0 nm (emission). Excitation wavelengths were 336 and 326 nm for DF/P and PF, respectively. Instrumental noise was 0.10 V root mean square. Signals at λ_{max} ranged between 8.8 and 9.1 V for DF/P measurements and were $\sim$2.2 V for PF measurements.

Sample chamber temperatures were maintained to within ±0.1 °C with a Haake FN constant temperature circulator monitored with an Omega Engineering Model 199 RTD digital thermometer. Benzophenone solutions for spectral measurements were contained in quartz electron paramagnetic resonance (EPR) tubes. The EPR tubes, 0.3 mm i.d., were inserted into a cylindrical quartz compartment through which the coolant traveled (methanol or distilled water) to ensure uniform sample temperature over a wide temperature range. Solution temperature was monitored immediately above the light beam path. Dry N_2 was used to flush the sample compartment and minimize condensation on sample cell and instrument optics.

Data Analysis. The PCA-SM calculation was performed on a spectrothermal matrix consisting of 90 total luminescence spectra representing 18 temperatures (-2.4 to 85.2 °C) containing 110 data points each (370-588 nm). The spectra were normalized so that the sum of intensities centered in each row was equal to unity. A Control Data Corp. Cyber 760 computer was employed. The mathematical treatment was performed on spectra that were not corrected for nonlinear instrumental response. However, resolved spectra were corrected and fractional contributions used in the van't Hoff treatment were based on corrected spectra. Correction factors were empirically obtained at 0.5-nm intervals by the method given by Parker[6] as previously described.[7]

Results and Discussion

Resolution of DF/P Spectra. The PCA-SM method for spectral resolution was proposed by Lawton and Sylvestre[8] and applied to the resolution of a spectrothermal matrix by Aartsma and co-workers.[9] Our extension of the method to the resolution of up to three nonequilibrating conformer fluorescence spectra has been described in detail,[1,7] and a preliminary report of the treatment of the benzophenone spectrothermal luminescence matrix has been reported.[1] The total emission spectra of benzophenone, $\mathbf{S}_i$, were regarded as linear combinations of DF and P spectra,

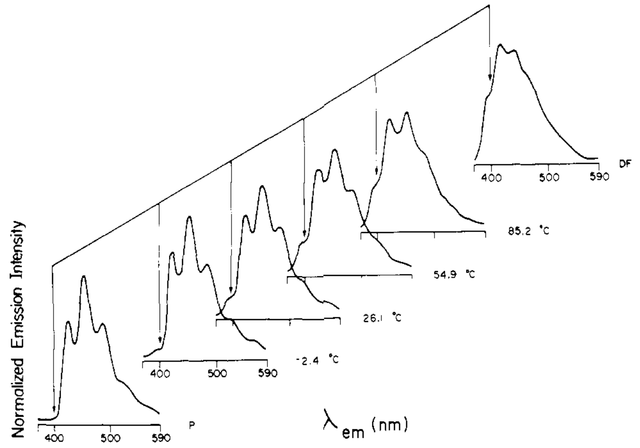

Figure 2. Representative benzophenone spectra at different temperatures and resolved P and DF spectra (uncorrected).

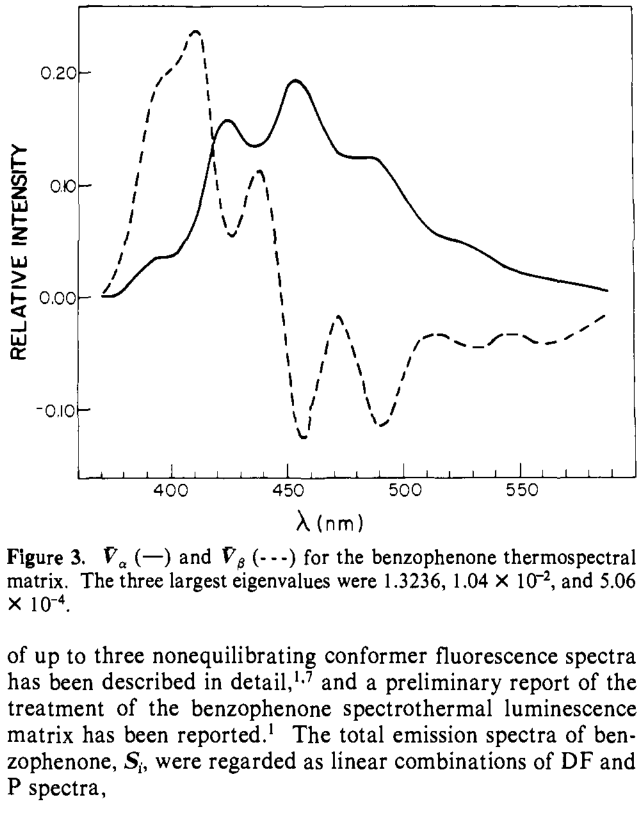

Figure 3. $\bar{V}_\alpha$ (—) and $\bar{V}_\beta$ (---) for the benzophenone thermospectral matrix. The three largest eigenvalues were 1.3236, 1.04×10^{-2}, and 5.06×10^{-4}.

$$\mathbf{S}_i = x_{ia}\mathbf{A} + x_{ib}\mathbf{B} \tag{1}$$

where $\mathbf{A}$ and $\mathbf{B}$ are pure DF and P spectra, respectively, and x_{ia} and x_{ib} are corresponding fractional contributions. The contribution of PF to the total emission is negligible because of its very small quantum yield (see below). The ratio of the fractional contributions of DF and P is proportional to the equilibrium constant, k_{-is}/k_{is}, which is temperature dependent. The spectra in Figure 2 illustrate the observed changes in the total emission as the temperature is changed. PCA treatment of the spectrothermal matrix yielded two eigenvectors, $\bar{V}_\alpha$ and $\bar{V}_\beta$, with significant eigenvalues (Figure 3). Experimental spectra were faithfully reconstructed as linear combinations of the eigenvectors,

$$\bar{S}_i = \alpha_i \bar{V}_\alpha + \beta_i \bar{V}_\beta \tag{2}$$

where α_i and β_i are the combination coefficients of the *i*th spectrum. The set of α_i,β_i fall closely on the normalization line defined by the eigenvectors (Figure 4).

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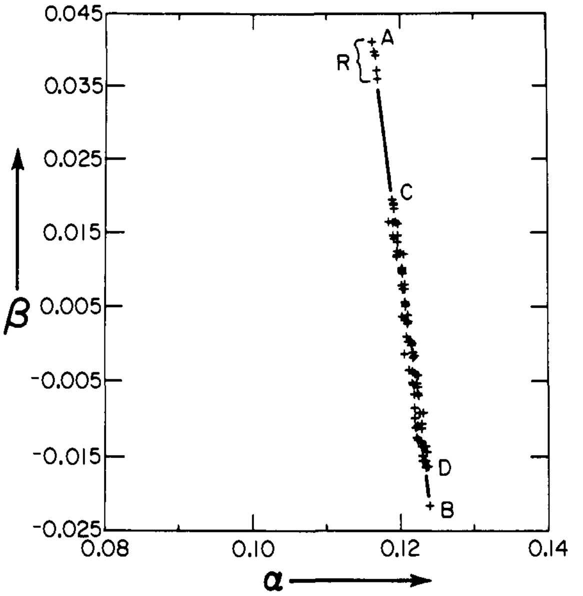

Figure 4. α,β plot for benzophenone matrix; the normalization line of $\bar{V}_\alpha$ and $\bar{V}_\beta$ is drawn through the points.

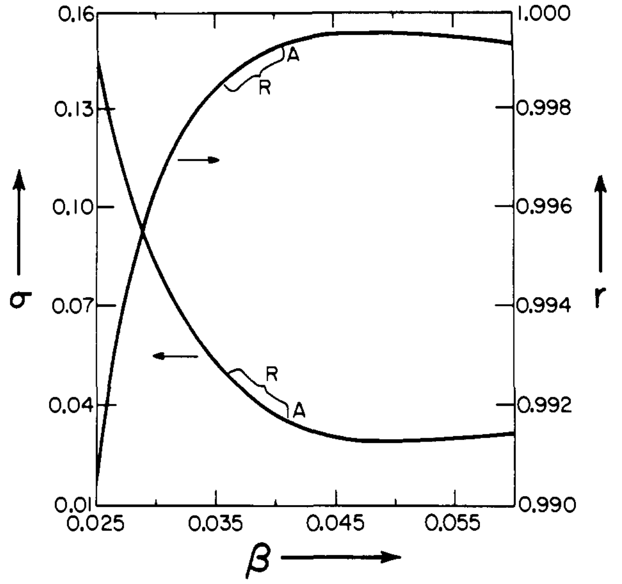

Figure 5. Plots of the standard deviation, σ, and the linear correlation coefficients, r, of the van't Hoff plot as a function of β.

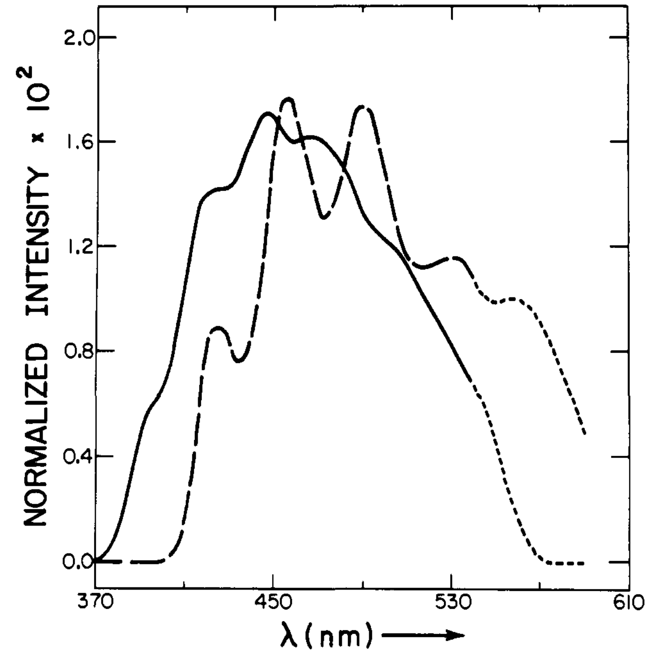

Figure 6. Corrected DF (—) and P (---) spectra; the spectra are not considered reliable at λ > 540 nm because the correction factors are too large.

Since the energy of the lowest excited singlet state of benzophenone is somewhat higher than the energy of the lowest triplet state it was reasonable to expect that the fluorescence spectrum would fall in a range of higher frequencies (shorter wavelengths) than the phosphorescence spectrum. Accordingly, only DF should contribute to the onset of the spectra and only P should contribute to the tail (cf. W_1 and W_2 regions in Figure 2, ref 1). If the spectra were devoid of instrumental noise, moving up from point C along the normalization line until the first zero intensity is attained in the tail region would give the pure DF spectrum *A* and moving down from point D until the first zero intensity is attained in the onset region would give the pure P spectrum ***B***. As described earlier, however, in practice, due to noise, this procedure often leads to premature reaching of the limiting pure component combination coefficients. The contribution of noise in determining the limits is minimized by going beyond the first zero intensity until stable spectral solutions are achieved which are independent of the number of zero or negligibly small negative intensities in the regions where the spectra do not overlap.[1] In the present case we found that 3 to 10 zero intensities in the onset region correspond to essentially the same coefficient point, B, which was therefore assigned to the pure P spectrum, Figures 2 and 6. Determination of the coefficient combination corresponding to the pure DF spectrum is less straightforward because it relies on intensities at relatively long wavelengths where the sensitivity of the photomultiplier employed in the measurements is relatively low. Noise in that region is more significant and the selection of the coefficients for DF is somewhat more difficult. The small region R on the normalization line corresponds to spectra with 4 to 11 negligibly small negative intensities in the tail region. It defines a range of acceptable choices of pure component coefficients for the DF spectrum. The possibility that the pure component coefficients might be closer to point C was eliminated by applying the additional criterion that acceptable coefficients for DF should lead to good linearity in the van't Hoff plot (cf., also, next section). Plots of the standard deviation and the linear correlation coefficient for van't Hoff plots versus the β coefficient selected for DF are shown in Figure 5. .Note that once β is selected α is defined by the normalization condition. It can be seen that region R corresponds to β values for which the standard deviation and the linear correlation coefficients are close to the minimum and maximum values, respectively. Using this criterion the outer limit of region R appeared to be the best choice for DF coefficients and was selected as point A. Spectra obtained for coefficient combinations beyond point A showed appreciable distortion in the tail region and were considered unacceptable although they led to slight improvement in the linearity of the van't Hoff plot (Figure 5). Selection of coefficients at the outer limits of region R had little effect on the appearance of the DF spectrum and a small effect on ΔH and ΔS values which has been included in the uncertainties given for these quantities. Uncorrected and corrected resolved DF and P spectra are shown in Figures 2 and 6, respectively.

The above analysis neglects possible nonlinear spectral changes, such as broadening with increasing temperature which, if significant, could invalidate the PCA–SM treatment. The importance of such effects was evaluated by treating submatrices comprised of smaller temperature regions (e.g., the upper 30 °C, middle 30 °C, and lower 30 °C, or the upper 45 °C and the lower 45 °C) separately. Though a subtle broadening in resolved spectra could be discerned with increasing mean temperature of the experimental spectra employed, the effect was small and did not affect ΔH and ΔS values seriously.

Rate Constants and the van't Hoff Plot. Previous applications of the van't Hoff plot to the temperature dependence of benzophenone luminescence were based on the scheme in Figure 1 and

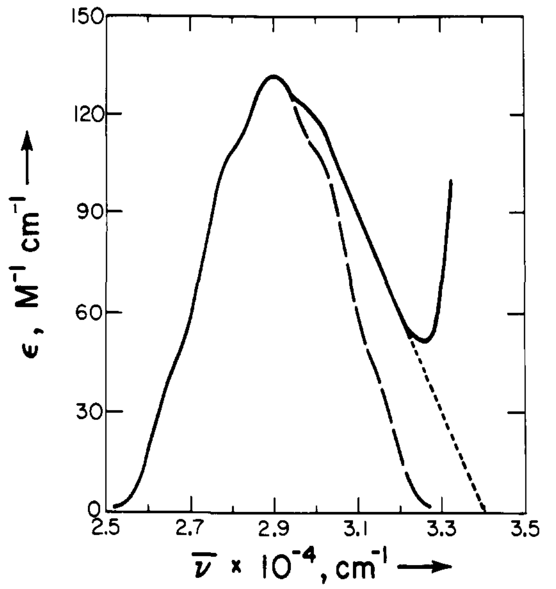

Figure 7. Absorption spectrum of benzophenone in CCl_4 showing two methods of isolating the $S_1 \leftarrow S_0$ band from the next transition (see text).

the conditions that S_1 and T_1 are fully equilibrated and prompt fluorescence is negligible at all temperatures employed, i.e., $k_{is} \gg k_f$ and $k_{-is} \gg k_p + k_d$.[2-5]

$$\frac{\phi_{DF}}{\phi_P} \approx \frac{k_f k_{-is}}{k_p k_{is}} = \frac{k_f}{k_p} K_{-is} \qquad (3)$$

Since fractional contributions, eq 1, are directly proportional to emission quantum yields, the same conditions give

$$\ln (x_a/x_b) = -(\Delta H/RT) + (\Delta S/R) + \ln (k_f/k_p) \qquad (4)$$

Direct measurements of the lifetime of benzophenone excited singlets in a variety of solvents, 7–12 ps, suggest that $k_{is} \simeq 10^{11}$ s^{-1} can be assumed for CCl_4.[10] An estimate of the singlet radiative rate constant, $k_f = 1.4 \times 10^5$ s^{-1}, which we had used earlier,[2] was incorrectly based only on the 0–0 band of the $S_1 \leftarrow S_0$ absorption spectrum of benzophenone.[11a] Approximate values of 10^6 (ref 11b) and 1.7×10^6 s^{-1} (ref 4b) have been based on the entire absorption band for the n,π^* transition. The availability of the DF spectrum allowed us to redetermine $k_f = (1.1 \pm 0.1) \times 10^6$ s^{-1} in CCl_4 using the Birks–Dyson equation.[12] Since the refractive index of CCl_4 is relatively insensitive to λ in the region of benzophenone's S_1–S_0 absorption and fluorescence,[13] the same value could be calculated from the Strickler–Berg equation.[14] The weak $S_1 \leftarrow S_0$ electronic band was isolated from the higher energy transition with which it overlapped with use of two extreme procedures (Figure 7). The first was based on the assumption that the low and high energy parts of the n,π^* transition bear mirror image symmetry to each other. It gave 0.97×10^6 s^{-1} as a lower limit for k_f. The second involved using a tangent on the higher energy portion of the transition to extend it into the region of the second absorption band. It gave 1.2×10^6 s^{-1} as the upper limit for k_f (cf. the procedure used for *N*-methylacridinium chloride in ref 14). Since $\phi_{PF} = k_f/k_{is}$ we estimate $\phi_{PF} \simeq 1.1 \times 10^{-5}$.

Assuming rapid equilibration between S_1 and T_1 in Figure 1 gives

$$\tau_t^{-1} = f_s k_f + f_t(k_p + k_d) \qquad (5)$$

where τ_t is the triplet lifetime and $f_s = (1 + K_{is})^{-1}$ and $f_t = K_{is}/(1 + K_{is})$ are the equilibrium fractions of S_1 and T_1 molecules, respectively.[15] The total luminescence yield, ϕ_L, is given by

$$\phi_L = \phi_{PF} + \phi_{DF} + \phi_P = \phi_{PF} + f_s k_f \tau_t + f_t k_p \tau_t \qquad (6)$$

where the last two terms give ϕ_{DF} and ϕ_P, respectively.[15] We had reported earlier $\phi_L = 1.5 \times 10^{-2}$ for $\sim 5 \times 10^{-3}$ M benzophenone in degassed CCl_4 at room temperature.[2] Since ϕ_{PF} contributes negligibly to ϕ_L, eq 3 follows from eq 6. At low temperatures $\phi_L = \phi_P$ and k_p can be calculated from ϕ_P/τ. Values of $k_p = 1.6 \times 10^2$ and 1.40×10^2 s^{-1} have been obtained from this ratio for

Table I. The Temperature Dependence of DF and P Contributions to Benzophenone Luminescence[a]

T, °C	x_a, %	x_b, %
-2.4	7.7 ± 0.6	92.3 ± 0.6
6.9	10.6 ± 0.8	89.4 ± 0.8
9.1	11.4 ± 0.9	88.6 ± 0.9
14.8	14.1 ± 1.1	85.9 ± 1.1
21.1	16.6 ± 1.3	83.4 ± 1.3
26.1	20.0 ± 1.6	80.0 ± 1.6
30.0	21.9 ± 1.8	78.1 ± 1.8
34.8	24.3 ± 2.0	75.7 ± 2.0
40.1	27.6 ± 2.3	72.4 ± 2.3
45.1	30.3 ± 2.5	69.7 ± 2.5
50.8	34.7 ± 2.9	65.3 ± 2.9
54.9	37.8 ± 3.2	62.2 ± 3.2
59.9	41.4 ± 3.6	58.6 ± 3.6
65.0	45.0 ± 3.9	55.0 ± 3.9
70.0	48.5 ± 4.3	51.5 ± 4.3
74.8	52.1 ± 4.6	47.9 ± 4.6
79.7	55.4 ± 5.0	44.6 ± 5.0
85.2	59.6 ± 5.4	40.4 ± 5.4

[a] Uncertainties indicate the change in x_a when point A is moved to the inner limit of region R in Figure 4.

Table II. S_1–T_1 Energy Splitting in Benzophenone

solvent	Δ*H*, kcal/mol	ref
CCl_4	6.3 ± 0.3	this work
CCl_4	4.4	2
C_6H_6	4.9	4c
polymer[a]	4.90 ± 0.10	5b
$C_6H_5CH_3$/EET[b]	6.3 ± 0.5	20

[a] Poly(chlorotrifluoroethylene). [b] Spectroscopically determined Δ*E*, absorption in toluene, phosphorescence, and phosphorescence excitation spectrum in 2:1:1 ether, ethanol, toluene at 77 K.

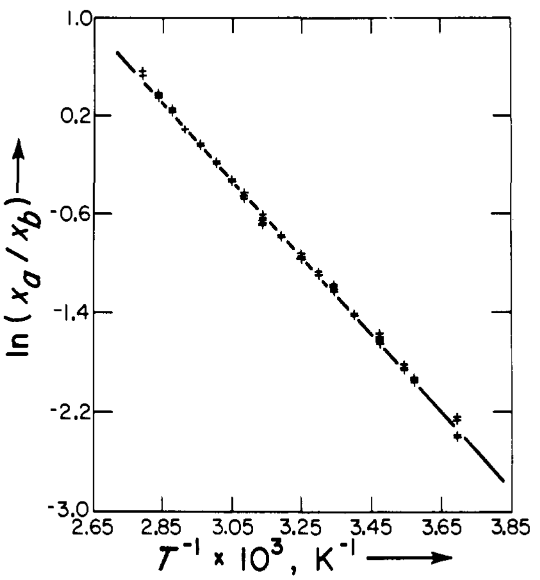

Figure 8. van't Hoff plot of the fractional contributions in Table I.

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benzophenone in an alcohol–ether glass at 77 K[16] and in polymethyl methacrylate films in the 100–180 K range,[17] respectively. A reported decrease in k_p as the temperature is raised above 180 K in the polymer medium, down to 50 s^{-1} at 300 K,[17] is of doubtful validity.[18] Adopting the highest value of $k_p = 1.6 \times 10^2\ s^{-1}$ for the CCl_4 solution seems justified in view of the possible enhancement of k_p due to solvent-induced spin–orbit coupling. It should be noted, however, that the addition of ethyl iodide has been shown not to enhance the intensity of the $T_1 \leftarrow S_0$ transition.[20]

Using A and B as pure component coefficients and correcting relative intensities for nonlinear instrumental response gives the spectra in Figure 6. The points on the normalization line in Figure 3 were adjusted to reflect the corrected spectra and the lever rule was applied to obtain the fractional contributions x_a and x_b for DF and P, respectively (Table I). The van't Hoff plot based on these fractional contributions, eq 5 (Figure 8), gives $\Delta H = 6.3 \pm 0.3$ kcal/mol and, with $k_p = 1.6 \times 10^2\ s^{-1}$ and $k_f = 1.1 \times 10^6\ s^{-1}$, $\Delta S = 0.7 \pm 1.0$ gibbs/mol for the $S_1 \leftarrow T_1$ direction. The ΔH value is larger than earlier estimates because previous van't Hoff treatments (Table II) underestimated the contribution of DF intensity at the frequencies used to monitor P intensity (see below).[2,4,5] However, ΔH now agrees exactly with the spectroscopically determined S_1–T_1 energy splitting.[20]

If the ΔS value reflected solely the change in multiplicity, $\Delta S = -R \ln 3 = -2.18$ gibbs/mol would be expected. The somewhat positive value obtained, though subject to the uncertainties in k_f and k_p, suggests a considerable gain in conformational freedom in going from T_1 to S_1. The relatively unresolved appearance of the DF spectrum compared to the P spectrum further suggests that the $S_1 \rightarrow S_0$ transition is accompanied by a larger geometry change than the $T_1 \rightarrow S_0$ transition. The entropy change for the triplet energy transfer equilibrium between benzophenone (donor) and the rigid molecule triphenylene (acceptor), $\Delta S = 4.3$ gibbs/mol, has been sensibly associated with a substantial increase in the conformational freedom of the benzophenone partner upon deexcitaton.[21] Accepting this assignment and including the multiplicity change term gives $\Delta S = 2.1$ gibbs/mol for the $T_1 \rightarrow S_0$ transition which can be combined with our ΔS for S_1/T_1 equilibration to give $\Delta S = 2.8$ gibbs/mol for the $S_1 \rightarrow S_0$ transition. An early MO calculation that did not differentiate between S_1 and T_1 states has predicted a significant shift toward a more nearly planar geometry upon n,π^* excitation of benzophenone.[22]

Due to hydrogen abstraction and other self-quenching interactions, the phosphorescence lifetime of benzophenone in CCl_4 depends on the concentration of benzophenone, [B]: $\tau^{-1} = \tau_0^{-1} + k_{sq}[B]$ where $\tau_0^{-1} = 1.1 \times 10^4\ s^{-1}$ and $k_{sq} = 3.3 \times 10^5\ M^{-1}\ s^{-1}$ at room temperature.[23] An alternative set of measurements for the dependence of τ^{-1} on [B] is considered suspect because it yielded a much larger τ_0^{-1} value[24] than obtained independently by other investigators.[2,23,25] It follows that $\tau = 7.9 \times 10^{-5}$ s for 5×10^{-3} M benzophenone. Since all the parameters in eq 6 are now assigned we can calculate $\phi_{DF} = 3.1 \times 10^{-2}$, $\phi_P = 1.26 \times 10^{-2}$, and $\phi_L = 1.57 \times 10^{-2}$ for $[B] = 5 \times 10^{-3}$ M in CCl_4 at 26.1 °C. It can be seen that ϕ_L is in excellent agreement with the experimental value, $\phi_L = 1.5 \times 10^{-2}$,[2] and that the assumption that ϕ_{PF} is negligible was justified. If τ were temperature independent, $\phi_P = 1.12 \times 10^{-2}$ would be predicted throughout the temperature range employed in our work and ϕ_{DF} would increase from 9.1×10^{-4} at −2.4 °C to 1.59×10^{-2} at 85.2 °C for 1.0×10^{-2} M benzophenone. The effect on ϕ_L would be an increase of more than a factor of 2. This can be compared with an observed increase of ~36% in the integrated area of the total luminescence as the temperature is raised from −2.4 to 85.2 °C. Apparently, the increase in ϕ_{DL} with increasing T is compensated partially by a decrease in τ. It is not known at this time whether the temperature effect in τ is due to changes in k_d or in k_{sq}, or in both of these constants. It is noteworthy, however, that in rigid media containing C–H bonds, τ decreases steeply with increasing T and leads to reduced ϕ_L at higher temperatures.[5b,17] On the other hand, for benzophenone vapor ϕ_L increases with increasing T.[3b]

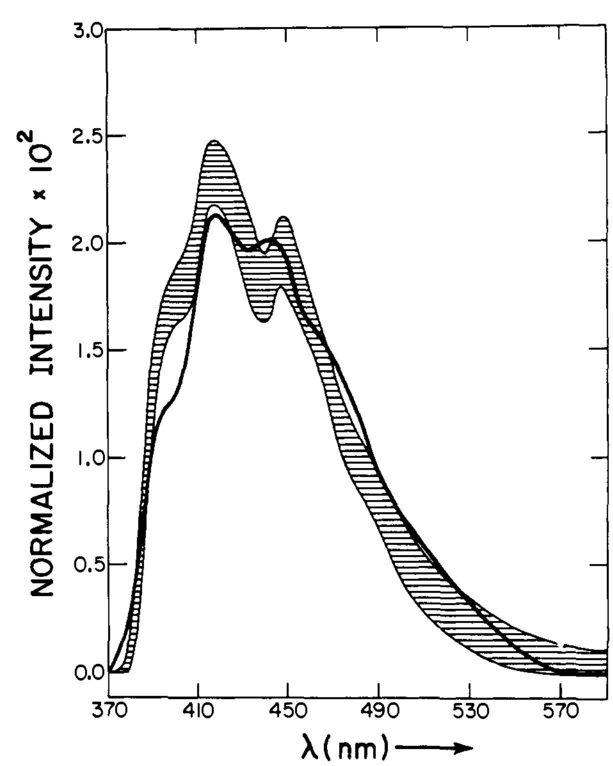

Figure 9. Comparison of PF (shaded area) and DF (dark line); spectra are uncorrected.

Prompt Fluorescence Spectrum. Time-resolved studies of benzophenone luminescence in benzene solution have yielded broad structureless fluorescence spectra that have been assigned to benzophenone's PF.[4] Our DF spectrum, though less well resolved than the P spectrum, shows vibronic structure and has a significantly different intensity profile than the time-resolved spectra. Since these differences might reflect errors in instrumental correction factors we measured the PF spectrum in CCl_4 using the same instrument and benzophenone concentration as were employed in the DF/P measurements. Since spectra of air-saturated solutions showed substantial P and, presumably, DF contributions, PF measurements were recorded in the presence of 0.1 M *trans*-1,3-pentadiene as an additional triplet quencher. Due to the low ϕ_{PF} of benzophenone, somewhat noisy spectra were obtained with the highest sensitivity setting of our fluorimeter. The contribution of random noise was reduced by averaging 20 separate single scan spectra. The resulting PF spectrum, depicted in Figure 9 as a narrow band reflecting the standard deviation at each wavelength, was reproducible in independent experiments. This PF spectrum, obtained by steady-state low-intensity excitation, is very different from Singer's time-resolved pulsed-excitation spectra,[4] and, though it bears a strong resemblance to our DF spectrum, it is obviously different from it (Figure 9). Since the same benzophenone concentration was employed for PF and DF experiments, the possibility that differences in self-absorption could give the false impression that the two spectra were different could be ruled out. Nonetheless, measurements were repeated at different benzophenone concentrations and it was experimentally established that the spectra in Figure 9 are not affected by

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self-absorption. This is consistent with the very low absorbance of the solutions in the region of absorption–fluorescence overlap. We also examined the possibility that the difference in the spectra may be due to our not having selected the correct point A on the normalization line (Figure 4). Spectra obtained for combination coefficients lying higher on the normalization line than point A showed no tendency to match the PF spectrum, but they appeared progressively more distorted due to increasing negative contributions of the P spectrum. As a final precaution, it was shown that the eigenvectors in Figure 3 fail to give a good fit for the PF spectrum. We conclude, therefore, that the differences between our PF and DF spectra are real and provide striking confirmation of the prediction made by Hochstrasser and co-workers that k_{is} from S_1 benzophenone competes with the vibrational relaxation (intramolecular and/or medium related) of this state.[26] Substantial difference in benzophenone T–T absorption spectra with 22- and 52-ps time delays following an 8-ps excitation pulse were observed. The change was attributed to the vibrational relaxation process in the triplet manifold which occurred in a time period of ~20 ps. It was reasoned that, since vibrational relaxation in S_1 should occur over a similar time period, the very large k_{is} for this state requires that intersystem crossing occur from vibrationally unrelaxed singlets. The difference between PF and DF spectra verifies this expectation since PF should arise from vibrationally unequilibrated S_1 states, whereas DF should originate from essentially relaxed S_1 states.

We now address the discrepancy between our PF spectrum and Singer's spectra.[4] Singer employed 8-ns laser pulses (337.1 nm) to excite 0.1 M solutions of a series of benzophenones in benzene solution. Spectra recorded with 10- or 100-ns sampling gate times with a delay of 0 ns (i.e., signal sampling was superimposed in time on the laser pulse) appeared identical and were structureless. Air-saturated solutions were employed to minimize the contribution of phosphorescence to the spectra. The spectra were said to be distorted on the high-energy side due to self-absorption and it was recognized that there were large contributions of a triplet–triplet annihilation component to the decay of benzophenone triplets[27] which gave rise to P-type delayed fluorescence in the spectra.[4c] Careful examination of spectra obtained from degassed solutions with variable delay times reveals that P-type delayed fluorescence is the dominant fluorescence obtained at delay times as long as 0.5 to 1 μs (see, for examples, Figures 4 and 5 in ref 4c). It seems likely, therefore, that the fluorescence spectra assigned by Singer to PF are actually due to P-type delayed fluorescence. Furthermore, since following triplet–triplet annihilation, emission from the product partners of excited singlet/ground state benzophenone molecules must occur prior to their diffusion apart, the emission can be regarded as fluorescence from the singlet excimer of benzophenone. Excimer emission is, of course, expected to be structureless and the difference between our spectra and Singer's spectra is thus explained. The assignment of a structureless PF spectrum to benzophenone had been questioned earlier.[28]

Our own attempts to time-resolve the PF spectrum of benzophenone using lower laser intensity (8-ns laser pulse; 0–10-ns gate) and benzophenone concentration than were employed in the earlier work[4a] resulted in noisy spectra that were always contaminated by P. The following kinetic analysis will show that our conditions and those employed earlier[4] could not have achieved time-resolution of PF from P.

Since the time durations of detection, time 0 to time t, were either 10 or 100 ns and $1/k_{is} \simeq 10$ ps, we assume that population of T_1 from S_1 is instantaneous. Since, furthermore, t is very small compared to the triplet lifetime, τ_t (94 μs and 286 ns in degassed[23,25] and air-saturated CCl_4, respectively), the decay of benzophenone triplets, $^3B^*$, during the detection gate time t is given by

$$\frac{[^3B^*]_t}{[^3B^*]_0} = e^{-t/\tau_t} \simeq 1 - \frac{t}{\tau_t} \qquad (7)$$

where $[^3B^*]_0$ and $[^3B^*]_t$ are the triplet concentrations at time 0 (i.e., the initial concentration following $^1B^*$ depletion in the ps time scale) and at time t, respectively. The P quantum yield in the 0 to t time interval is given by

$$\phi_P(t) = \phi_P \frac{[^3B^*]_0 - [^3B^*]_t}{[^3B^*]_0} \qquad (8)$$

where $\phi_P = k_P\tau_t$ since the intersystem crossing quantum yield is unity. Combining eq 7 and 8 gives

$$\phi_P(t) = k_P t \qquad (9)$$

It follows that during the detection time gate period the ratio between P and PF is given by

$$\frac{\phi_P(t)}{\phi_{PF}} = \frac{k_P t}{k_f\tau_f} = (1.4_5 \times 10^7)t \text{ s}^{-1} \qquad (10)$$

Experimental estimates of ϕ_{PF} of 4×10^{-6} for CCl_4 solution[25] and 1×10^{-5} for a hydrocarbon glass at 5 K[28] have been published. They are consistent with our calculated value of $k_f\tau_f \simeq 1.1 \times 10^{-5}$, which together with $k_P = 1.6 \times 10^2$ s^{-1} gives the relationship in eq 10. It follows that for $t = 10$ ns nearly 13% of the time-resolved luminescence should be P for either degassed or air-saturated solutions, and for $t = 100$ ns more than half of the luminescence should be P. Our failure to fully time resolve PF from P is thus understandable. On the other hand, the absence of P from Singer's spectra confirms our suspicion that his spectra were dominated by a stronger P-type excimer fluorescence.

Under steady-state excitation conditions eq 10 must be modified to

$$\frac{\phi_P}{\phi_{PF}} = \frac{k_P\tau_t}{k_f\tau_f} = (1.4_5 \times 10^7)\tau_t \text{ s}^{-1} \qquad (11)$$

Assuming a rate constant of 5×10^9 M^{-1} s^{-1} for the quenching of benzophenone triplets by *trans*-1,3-pentadiene we estimate $\tau_t \simeq 2$ ns in the presence of 0.1 M diene. It follows that P should contribute less than 3% to the emission spectrum we assigned to PF.

Morris and Williams have assigned the PF spectrum of vibrationally relaxed benzophenone singlets to a narrow spectral band with $\nu_{max} \simeq 375$ nm.[28] Under their conditions (methylcyclohexane–isopentane mixture, 5 K) the phosphorescence spectrum shows a well-defined progression of broad vibrational bands and it is not clear why the fluorescence spectrum should only show the 0–0 band. Also the failure of these authors to observe PF clearly at temperatures higher than 10 K is inconsistent with our observations.

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Registry No. Benzophenone, 119-61-9; carbon tetrachloride, 56-23-5; *trans*-1,3-pentadiene, 2004-70-8.

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