Temperature Dependence of the Fluorescence Lifetime of Benzene in Cryogenic Solutions†

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Fluorescence lifetimes for C6D6 in various hydrocarbon solvents have been measured as a function of concentration and temperature. For the solvents ethylene, ethane, and propane it is found that at low concentrations (~0.3 ppm or ~4 x 10^-8 mol/L) the fluorescence lifetime is roughly temperature independent (90 ≤ T ≤ 220 K) and equal to the gas-phase value of ~150 ns. As the concentration is increased (1 ≤ c ≤ 100 ppm), the lifetime decreases as temperature is increased, reaching a minimum value at about 150 K of roughly 70-100 ns, depending on the concentration. As the temperature is increased from 150 to 220 K, the lifetime increases to well over 100 ns. These trends can be understood on the basis of a monomer/excimer kinetic model in which benzene excimers form at low temperature and break apart at high temperature to regenerate the excited-state and ground-state monomers. In propene and 1-butene solvents, such behavior is not observed most likely due to solvent triplet-state quenching of the excited 1B2u benzene monomer.

Introduction
The study of molecular electronic spectra of solute molecules in cryogenic molecular liquids has begun to draw increasing attention in recent years.1 Fluorescent and phosphorescent probe molecules can provide information on local structure and microdynamics of chemical systems in liquid solution.2 Moreover, even at low concentrations (1 ppm or ~1.5 x 10^-9 mol/L) absorption and emission spectra are intense enough to provide good signal-to-noise detection ratios. Cryogenic liquids reduce the spectral congestion associated with hot bands and quite often solvent effects induce forbidden transitions by lowering the effective solute symmetry. Benzene, as a solvent probe in several cryogenic liquids, has proved helpful in studying solvent–solute interactions and liquid-state structure.3,4 Cryogenic small-molecule liquids are employed in this research because they are simple but still molecular, they are good solvents for organic molecules, they possess a wide liquid range, and their low temperature allows for sharp spectroscopic probe features.5 Benzene is a reasonable probe system because of its high symmetry, well-known spectra and kinetics, and solubility.

In the present study, fluorescence lifetimes of the first excited singlet state of benzene are reported in several cryogenic liquids. The solvents employed in these studies are methane, ethane, ethylene, propane, propene, and 1-butene. The experimental results are explained on the basis of a monomer/dimer (excimer) kinetic model. At low temperature the “cage” structure of the liquid provides an effective mechanism for the formation of an excimer once

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a ground-state benzene molecule has diffused to and is trapped in a cage in which there also resides an excited-state molecule. At high temperature the lifetime of this cage structure is significantly reduced by the large thermal energy available to the molecules. Dissociation of these excimers repopulates the excited-state monomer and an increase in the fluorescence lifetime is observed at high temperature. It is further demonstrated that the formation of excimers is a diffusion-controlled process with a high probability of excimer formation on each excited-state/ground-state benzene pair encounter. It is postulated that this high cross section for formation is associated with a solvent cage or coordination (solvent shell) structure. There is some evidence that \( ^1B_{2u} \) benzene may also relax through a high-efficiency nonradiative pathway accessible at energies \( \sim 2500 \text{ cm}^{-1} \) above the zero-point energy of the \( ^1B_{2u} \) state; this route is only open to benzene in liquids or high-pressure gases near or above room temperature, however.

**Experimental Section**

Sample preparation and the instrumental setup have been described in other reports.\(^5,6\) \( \text{C}_6\text{D}_6 \) (Aldrich Gold Label) and \( \text{C}_6\text{H}_6 \) (Fisher Gold Label) are further purified by vacuum distillation over potassium to remove water and other oxygen-containing impurities. Solvents are all research grade of the highest obtainable commercial purity. All solvents are vacuum distilled and passed through molecular sieve, oxygen scavenger (Ridox), and activated charcoal. Samples are premixed in a 7-L stainless-steel can. Concentrations are regulated on the basis of the known vapor pressure of \( \text{C}_6\text{H}_6/\text{C}_6\text{D}_6 \) in calibrated volumes and fixed gas-phase volume/pressure measurements for the solvent. Frequency-doubled pulses from a Nd:YAG laser (Quanta-Ray DCR-1) are used to pump a rhodamine 610 dye laser. The output of the dye laser is frequency doubled into the UV; the UV radiation is then Raman shifted in a high-pressure \( \text{H}_2 \) (270 psi) cell. The first stimulated anti-Stokes line from the Raman cell is appropriate for pumping vibronic transitions of the \( ^1B_{2u} \rightarrow ^1A_{1g} \) manifold in various cryogenic solvents. The energy of this unfocused beam at the sample is roughly 1–2 mJ/pulse, the pulse width is \( \sim 5 \text{ ns} \), and the line width is \( \sim 0.5 \text{ cm}^{-1} \). Dispersed fluorescence is detected by an RCA C31000M photomultiplier tube, the signal from which is then processed by a boxcar averager (PAR 162/164) which interfaces to a desk-top computer (HP9845S). A relaxation curve is obtained as the boxcar is scanned by a ramp voltage from the computer. Typical scan times are 10 min for a 500-ns scanning range. The decay curves obtained are then fitted by a single exponential decay function with an adjustable base line. The standard deviation of a number of measurements of the decay times for a given sample and temperature based on a complete fit to the experimental decay curves is always better than 5%. Since the signals are dispersed and the detection wavelength is at the peak of a monomer transition, only the monomer fluorescence lifetime is of concern.

**Results**

Although we have data for both \( \text{C}_6\text{H}_6 \) and \( \text{C}_6\text{D}_6 \) only those results referring to \( \text{C}_6\text{D}_6 \) will be presented and discussed in this paper. In all respects, both molecules give essentially the same information. Decay curves for the benzene fluorescence in liquid solutions (\( \text{C}_6\text{D}_6/\text{C}_6\text{H}_6 \)) are shown in Figure 1. Within the stated standard deviation, as determined by computer fitting of the entire decay curve after the first 10 ns, all decay curves could be modeled by a single exponential function.

![Figure 1](image1.png)

**Figure 1.** Fluorescence intensity as a function of time for 4 ppm \( \text{C}_6\text{D}_6 \) in liquid \( \text{C}_6\text{H}_6 \) at 90, 150, and 180 K. The lines through the data are computer least-squares fits to the decay function with relaxation times as indicated in the figure.

![Figure 2](image2.png)

**Figure 2.** Temperature dependence of the fluorescence lifetime of \( \text{C}_6\text{D}_6 \) in \( \text{C}_6\text{H}_6 \) ((X) 0.3, (A) 18, and (O) 90 ppm; at 90 K 1 ppm \( \sim 1.9 \times 10^{-4} \text{ mol/L} \)).

![Figure 3](image3.png)

**Figure 3.** Temperature dependence of the fluorescence lifetime of \( \text{C}_6\text{D}_6 \) in \( \text{C}_6\text{H}_6 \) ((X) 0.3, (A) 18, and (O) 90 ppm; at 90 K 1 ppm \( \sim 1.3 \times 10^{-4} \text{ mol/L} \)).

The resulting lifetimes of the \( ^1B_{2u} \) state of benzene in various solvents as a function of temperature are shown in Figures 2–4. For the \( \text{C}_6\text{D}_6/\text{C}_6\text{H}_6 \), \( \text{C}_6\text{D}_6/\text{C}_6\text{H}_8 \), and \( \text{C}_6\text{D}_6/\text{C}_6\text{H}_{12} \) systems, the lifetime of the \( ^1B_{2u} \) state shows only a small dependence on temperature at low concentrations (\( \sim 0.3 \text{ ppm} \)). This change, over the range 90–220 K, is roughly 10% (\( \sim 150–130 \text{ ns} \)). At low temperatures,
the fluorescence lifetimes approach the value of the low-
pressure gas. Temperature dependence of the lifetime be-
comes prominent at higher concentrations, however. At
higher temperatures with moderate concentration, the
lifetime falls to a minimum value. As the temperature
further increases, the lifetime begins to increase (see
Figures 2-4).

In order to determine the cause of this lifetime behavior
with concentration and temperature, we added $6 \times 10^{-4}$
moL of $\text{O}_2$ to the $\text{C}_6\text{D}_6/\text{C}_2\text{H}_4$ system. An overall shorter
lifetime (about 20%) for the benzene emission was ob-
erved. The same temperature dependence of lifetimes
was detected, however. Since $\text{O}_2$ is an effective triple-
state quencher, this observation tends to eliminate the triple-
state benzene as an effective cause of such behavior.
Both thermal depopulation of $3\text{B}_2u$ to $1\text{B}_2u$ and triplet-
triplet annihilation mechanisms are thus not dominant
(although they may be present) in the overall kinetic
processes. Moreover, linear dependence of the fluores-
cence intensity on the input laser power also seems to rule out
diffusion-controlled triplet-triplet annihilation processes.

The lifetime of the $1\text{B}_2u$ state in $\text{C}_6\text{H}_6$ and $\text{C}_3\text{H}_4$ was
also studied as a function of temperature and concentra-
tion. The behavior of the fluorescence intensity as a
function of time and temperature is quite different for
these two solvents from that found for $\text{C}_2\text{H}_4$, $\text{C}_3\text{H}_4$, and
$\text{C}_6\text{H}_6$. The lifetime of the $\text{B}_2u$ state shows a dramatic
decrease as temperature is increased; no recovery of the
low-temperature lifetime is observed even at the highest
$91\text{ K}$ $1$ ppm in $\text{C}_2\text{H}_4$ is $\sim 1.3 \times 10^{-5}$ moL/L and in $\text{C}_6\text{H}_6$ is $\sim 1.4 \times 10^{-5}$
moL/L.
moreover, that the observed cryogenic liquid-state lifetime
is about the same as the longest vibronic-level lifetimes
measured for the $\text{B}_2u$ state ($\sim 150$ ns). Thus, it seems
reasonable to assume that the electronic-state lifetime of
$\text{B}_2u$ is closely approximated by that lifetime observed in
dilute cryogenic liquids.

The similar values of the fluorescence lifetimes of benzene in low-temperature liquids and in the low-pressure
gas phase are consistent with the nearly identical quantum
yields under these two very different sets of conditions. A
graphical extrapolation of the low-temperature, low-
concentration liquid lifetime to room temperature yields
a lifetime of $\sim 110$ ns; this is much longer than the usually
reported 20-30 ns lifetime for room-temperature liquid. The
fluorescence lifetimes of the high-pressure gas typi-
cally fall between these two values (20-110 ns). These
observations indicate that the relaxation rate from the zero-
point level of the excited $\text{B}_2u$ state of benzene is largely
an intramolecular property not grossly perturbed by
collisions. Once the excited molecule is relaxed to this
level, further collisions do not readily induce direct re-
laxation to the lowest electronic state. However, collisions
can activate the $\text{B}_2u$ zero-point molecules to higher vi-
brational levels in the $\text{B}_2u$ manifold—in particular, to the
level at $\sim 2500 \text{ cm}^{-1}$ which reportedly opens a new non-
radiative channel for relaxation. At low temperature,
thermal collisional activation to this fast relaxation path-
way can be neglected; consequently, the relaxation rate is
slow in low-pressure gases at room temperature as the rate
of activation through high-energy collisions is quite slow.
Thus, the conclusion is that low-temperature liquid solu-
tions of benzene and dilute gas-phase benzene should have
nearly the same $\text{B}_2u$ electronic-state relaxation times, while
room-temperature benzene solutions should have much
shorter relaxation times. The high frequency of collision
and high thermal energy in room-temperature liquids and
high-pressure gases effectively shortens the fluorescence
lifetime of benzene through collision-induced vibrational
activation. The general implication of this line of reason-
ing is that the low-temperature liquid can be construed as
providing a relatively “collision-free” structure (cage) for
the solute. On the other hand, the high thermal energy
of room-temperature liquids generates high collision rates
(quickly varying or oscillating structures) with many of

Discussion

It is known that different vibronic levels of the $\text{B}_2u$ state
of benzene have difference lifetimes in the gas phase at
low pressures. An increase in the gas pressure will result
in a thermally equilibrated vibronic manifold from which
one observes an average lifetime for all vibronic levels. In
order to measure the lifetime of the zeroth vibrational level
of the $\text{B}_2u$ state, one must employ very low pressures with
excitation through a hot band transition. Such studies give
a low-pressure electronic lifetime of $\sim 160$ ns. However,
in cryogenic liquid solutions it has been demonstrated that
all emission comes from the zero-point state of $\text{B}_2u$ and,

(7) (a) K. G. Spears and S. A. Rice, J. Chem. Phys., 55, 5561 (1971);
(b) A. S. Abramson, K. G. Spears, and S. A. Rice, ibid., 56, 2291 (1972).
(10) J. B. Birks, C. L. Braga, and M. D. Lumb, Proc. R. Soc. London,
At higher temperatures benzene; nomer/excimer systems and gives an explanation of the fluorescence rate (s-1) of the monomer, the fluorescence science, London, 1970.

In which dimer (excimer) benzene; benzene; benzene; benzene in cryogenic liquids, there is a much larger temperature leads to an increase in the observed fluorescence lifetime. This anomalous behavior in the cryogenic liquids C2H4, C2H6, and C3H8 is consistent with the formation of the excimer from an excited monomer and a ground-state monomer.

Figure 6 shows the rate processes considered for the monomer/excimer formation and decay.

\[ k_{DM} = k_{DM}^0 + e^{-\Delta E_{M} / k_{B} T} \]
\[ k_{ID} = k_{ID}^0 + e^{-(\Delta E_{I} - \Delta E_{F}) / k_{B} T} \]
\[ k_{DM} = k_{DM}^0 + e^{-(\Delta E_{E} - \Delta E_{F}) / k_{B} T} \]

In the temperature range of interest, this term can be written as:

\[ k_{IM} = k_{IM}^0 + k_{DM} \theta = k_{DM}^0 + k_{DM} \theta \]
\[ k_{ID} = k_{ID}^0 + k_{DM} \theta \]
\[ k_{DM} = k_{DM}^0 + k_{DM} \theta \]

These collisions being of high energy, perhaps due to multiple simultaneous events.

In addition to this small temperature dependence for the fluorescence lifetime of very dilute (\( \sim 5 \times 10^{-6} \) mol/L) benzene in cryogenic liquids, there is a much higher temperature dependence of this lifetime for high-concentration solutions (2 \( \times 10^{-6} \leq 2 \times 10^{-3} \) mol/L). Higher concentrations yield, in general, shorter lifetimes. This indicates that another quenching process begins to operate which must be at least a bimolecular one. These data also show (Figures 2-4) that, as temperature increases, the relaxation time reaches a minimum value; further increase of the temperature leads to an increase in the \( 1B_{2g} \) fluorescence lifetime. This anomalous behavior in the cryogenic liquids \( C_2H_4, C_2H_6 \) and \( C_3H_6 \) is consistent with the formation of bimolecular exchangers which quench the excited monomer. At higher temperatures (\( \sim 150 \leq T \leq 220 \) K), the dissociation of exchangers repopulates the excited \( 1B_{2g} \) state of the monomer, thereby leading to an increase in the observed fluorescence lifetime.

In order to demonstrate that the above process is the correct description for the observed lifetime behavior, it is necessary to present a kinetic scheme which, for specific values of the parameters, will generate such complex behavior with temperature and solute concentration. The discussion below follows closely the discussion of Birks. Figure 6 shows the rate processes considered for the monomer/excimer systems and gives an explanation of the notation. For pulsed excitation, the rate equations governing the excited-state monomer and excimer are

\[ d[M^*]/dt = -k_{FM} + k_{DM}[M] + k_{DM}[D^*] \]
\[ d[D^*]/dt = k_{DM}[M^*] - (k_{FD} + k_{ID} + k_{MD})[D^*] \]

in which \([M]\) is the concentration (mol/L) of ground-state benzene; \([M^*]\) is the concentration (mol/L) of excited-state benzene; \([D^*]\) is the concentration (mol/L) of excited-state dimer (excimer) benzene; \(k_{FM}, k_{FD}, k_{IM}, k_{ID}\) and \(k_{MD}\) are the fluorescence rate (s-1) of the monomer, the fluorescence rate of the excimer, the total nonradiative rate of monomer, and the total nonradiative rate of the excimer, respectively; \(k_{DM}[M]\) is the rate of formation of the excimer from the combination of an excited monomer and a ground-state monomer; and \(k_{MD}\) is the dissociation rate of the excimer to form an excited monomer and a ground-state monomer.

Applying the initial conditions that at \( t = 0, [M^*] = [M^*]_0 \), and \([D^*] = 0\), one can write the solutions of eq 1 and 2:

\[ [M^*] = [M^*]_0 (e^{-\lambda_2 t} + A e^{-\lambda_1 t}) \]
\[ [D^*] = [M^*]_0 \frac{k_{DM}[M]}{\lambda_2 - \lambda_1} (e^{-\lambda_1 t} - e^{-\lambda_2 t}) \]

in which

\[ x = k_{FM} + k_{DM}[M] \]
\[ y = k_{FD} + k_{MD} \]
\[ k_{IM} = k_{FM} + k_{ID} \]
\[ k_{ID} = k_{FD} + k_{IM} \]
\[ A = (x - \lambda_1)/(\lambda_2 - x) \]

\[ \lambda_{1,2} = (x + y)/2 \pm \sqrt{(y - x)^2 + 4 k_{DM} k_{MD}[M]} \]

The temperature dependence of the above rate constants can be written as (10)

\[ k_{IM} = k_{IM}^0 + k_{DM}^0 e^{-\Delta E_{M} / k_{B} T} + k_{DM}^0 e^{-\Delta E_{M} / (k_{B} T)} \]
\[ k_{ID} = k_{ID}^0 + k_{DM}^0 e^{-\Delta E_{I} / k_{B} T} \]
\[ k_{DM} = k_{DM}^0 e^{-\Delta E_{E} / (k_{B} T)} \]
\[ k_{MD} = k_{MD}^0 e^{-(\Delta E_{E} - \Delta E_{F}) / k_{B} T} \]

These collisions are temperature independent. In the above equations, \( k_{IM} \) is the nonradiative rate of the \( 1B_{2g} \) excited monomer, \( k_{DM} \) is the temperature-independent portion of \( k_{IM} \), and \( k_{ID} \) is the frequency factor of the temperature-dependence part of \( k_{IM} \) at low temperature. The second term in eq 5 is about 10% of the total relaxation rate \( k_{IM} \) over the range 90-220 K for 0.3 ppm (5 \( \times 10^{-6} \) mol/L) solutions. The third term on the right of eq 5 is the rate of the nonradiative pathway that apparently appears at \( \sim 2500 \) cm\(^{-1}\) above the zero-point level of the \( 1B_{2g} \) state.

In the temperature range of interest, this term can be ignored. \( k_{ID} \) is the nonradiative rate of the excimer and includes two terms: one temperature dependent and one temperature independent. \( k_{DM} \) presents a diffusion process with an activation energy \( \Delta E_{I} = \Delta E_{F} \) the diffusion activation energy of the solvent. Finally, \( k_{MD} \) is the rate of breakup of the excimer which is also a thermally activated rate with activation energy \( \Delta E_{E} \). It is clear from the above discussion that the second term in eq 5 is small (\( \Delta E_{M} \) is small) and plays only a minor role in the overall decay rate for the \( 1B_{2g} \) monomer excited state.

Excimer fluorescence is not observed in any of the solutions, most likely due to its width, and therefore, \( k_{ID} \) and \( k_{ID} \) need to be evaluated from other parameters. The rate of formation of exchangers, \( k_{DM}[M] \), is a diffusion-controlled process and the activation energy for excimer formation \( \Delta E_{I} \) is equal to the activation energy for diffusion.

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TABLE I: Estimates of the Rate Constants for C\textsubscript{6}D\textsubscript{6} Fluorescence in C\textsubscript{6}H\textsubscript{6} Solvent as a Function of Temperature\textsuperscript{a}

<table>
<thead>
<tr>
<th>T, K</th>
<th>C\textsubscript{b}, mol/L</th>
<th>k\textsubscript{DM}/k\textsubscript{MD}\textsuperscript{c}</th>
<th>k\textsubscript{M}, s\textsuperscript{-1}</th>
<th>k\textsubscript{DM}[M], d s\textsuperscript{-1}</th>
<th>k\textsubscript{D}, e s\textsuperscript{-1}</th>
<th>k\textsubscript{MD}, s\textsuperscript{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>90</td>
<td>7.6 x 10\textsuperscript{-3}</td>
<td>8.1 x 10\textsuperscript{7}</td>
<td>~6 x 10\textsuperscript{4}</td>
<td>4.0 x 10\textsuperscript{5}</td>
<td>~2 x 10\textsuperscript{4}</td>
<td>1.0 x 10\textsuperscript{4}</td>
</tr>
<tr>
<td>120</td>
<td>1.7 x 10\textsuperscript{-3}</td>
<td>6.6 x 10\textsuperscript{4}</td>
<td>~6 x 10\textsuperscript{4}</td>
<td>2.3 x 10\textsuperscript{5}</td>
<td>~2 x 10\textsuperscript{4}</td>
<td>6.0 x 10\textsuperscript{4}</td>
</tr>
<tr>
<td>150</td>
<td>9.5 x 10\textsuperscript{-4}</td>
<td>6.2 x 10\textsuperscript{2}</td>
<td>6.3 x 10\textsuperscript{4}</td>
<td>6.5 x 10\textsuperscript{4}</td>
<td>6.2 x 10\textsuperscript{4}</td>
<td>4.1 x 10\textsuperscript{4}</td>
</tr>
<tr>
<td>160</td>
<td>5.7 x 10\textsuperscript{-3}</td>
<td>3.2 x 10\textsuperscript{2}</td>
<td>~6 x 10\textsuperscript{4}</td>
<td>6.5 x 10\textsuperscript{4}</td>
<td>6.2 x 10\textsuperscript{4}</td>
<td>4.1 x 10\textsuperscript{4}</td>
</tr>
<tr>
<td>170</td>
<td>1.1 x 10\textsuperscript{-3}</td>
<td>1.2 x 10\textsuperscript{2}</td>
<td>~6 x 10\textsuperscript{4}</td>
<td>6.5 x 10\textsuperscript{4}</td>
<td>6.2 x 10\textsuperscript{4}</td>
<td>4.1 x 10\textsuperscript{4}</td>
</tr>
<tr>
<td>180</td>
<td>1.8 x 10\textsuperscript{-3}</td>
<td>5.3 x 10\textsuperscript{1}</td>
<td>~6 x 10\textsuperscript{4}</td>
<td>6.5 x 10\textsuperscript{4}</td>
<td>6.2 x 10\textsuperscript{4}</td>
<td>4.1 x 10\textsuperscript{4}</td>
</tr>
</tbody>
</table>

\textsuperscript{a} See text and Figure 6 for details concerning the processes and the overall scheme. \textsuperscript{b} Calculated from concentration dependence of the fluorescence lifetime at each temperature. \textsuperscript{c} Calculated from $e(\beta/k(T) - \Delta H(T) + \Delta S)$ \textsuperscript{d} Assumes 50 ppm (5.7 x 10\textsuperscript{-4} mol/L) of C\textsubscript{6}D\textsubscript{6} in C\textsubscript{6}H\textsubscript{6} and viscosity data of C\textsubscript{6}H\textsubscript{6}. \textsuperscript{e} Calculated from $k\textsubscript{D} = k\textsubscript{M}(1/C\textsubscript{b})(k\textsubscript{MD}/k\textsubscript{DM})$ at high temperature. \textsuperscript{f} Estimated order of magnitude.

The observed anomalous behavior for fluorescence in low-temperature liquids. It should be kept in mind that this discussion does not represent a proof of the scheme but shows that the experimental results can be fitted within the scope of the kinetic model. Not all rate constants could be evaluated from $\lambda_1$ and $\lambda_2$ because only single exponential decays are observed and no excimer fluorescence was found. More will be said about this at the end of this section.

In the low-temperature range (T ≤ 120 K), for which $k\textsubscript{MD}[M] > k\textsubscript{MD}$ and $k\textsubscript{D} > k\textsubscript{MD}$ can be assumed, expressions for $\lambda_1$ and $\lambda_2$ can be approximated to

$$\lambda_1 \sim x \quad \lambda_2 \sim y$$

and $A = (x - \lambda_1)/(\lambda_2 - x)$ approaches 0. Under these conditions, the effective decay rate of the excited monomer can be described as a single exponential decreasing function. This rate is $k \sim k\textsubscript{MD}[M]$. At low concentrations, for which bimolecular reactions can be neglected, the decay rate $k \sim k\textsubscript{MD}$ for benzene. The results show that $k\textsubscript{MD}$ is only slightly temperature dependent (Figures 2-4). Increase of the solute concentration makes the bimolecular quenching more important. The difference between the decay rates of two different concentration solutions indicates a process with an associated activation energy approximately equal to the activation energy for the diffusion process calculated from solvent viscosity data. Thus, $k\textsubscript{MD}$ is roughly equal to the diffusion rate constant, excimer formation is diffusion controlled, and the probability of excimer formation from the collision of an excited and ground-state monomer is close to unity. This efficient formation of the excimer can be realized in terms of a solvent cage trapping of the pair of molecules. At low temperature, once such a solvent structure traps the excited and ground-state molecules, reseparation is difficult due to the surrounding solvent shell potential well.

At higher temperature ($T \sim 150$ K), for which the reverse conditions exist ($k\textsubscript{MD}[M] > k\textsubscript{MD}$ and $k\textsubscript{MD} > k\textsubscript{D}$), the effective rate parameters are

$$\lambda_1 \sim \frac{k\textsubscript{MD}[M] + k\textsubscript{D}[M]}{k\textsubscript{MD}[M]}$$

$$\lambda_2 \sim \frac{k\textsubscript{MD}[M] + k\textsubscript{D}[M]}{k\textsubscript{MD}[M]} = \frac{k\textsubscript{MD}[M]}{k\textsubscript{D}[M]}$$

$$A = 1 + \frac{k\textsubscript{MD}[M]}{k\textsubscript{MD}[M]} - \frac{k\textsubscript{D}[M]}{k\textsubscript{MD}[M]}$$

It is clear that $\lambda_2 \gg \lambda_1$ and $A$ is only about unity. As one can see from Table I, the components of the second term in eq 3 will decay in a few nanoseconds. Thus, $\lambda_1$ is the same order of magnitude as $k\textsubscript{MD}$ and this will be the observed effective decay rate based on the experimental time resolution. Physically this condition implies that the monomer and excimer are in dynamic equilibrium; $\lambda_1$ is then the rate at which electronic excitation is lost from the system with $[M^*]$ and $[D^*]$ in equilibrium.

All the above rate constants are temperature dependent as discussed in eq 5-8. However, the intrinsic temperature dependence of $k\textsubscript{MD}$ is weak and we can assume the same is true for $k\textsubscript{D}$; to a first approximation we will neglect the two temperature-dependent components of $k\textsubscript{MD}$ and $k\textsubscript{D}$. In order to determine the residual temperature behavior of $\lambda_1$, one can obtain the temperature deviation of $\lambda_1$ approximately as

$$d\lambda_1/dT = (k\textsubscript{MD}[M](k\textsubscript{MD} - k\textsubscript{D})) \times (\Delta E_2 - \Delta E_1)/(k\textsubscript{D}T^2)/(k\textsubscript{MD}[M] + k\textsubscript{D}[M])^2$$

Since every term in this expression is positive and $\Delta E_2 > \Delta E_1$, the fact that $k\textsubscript{D} > k\textsubscript{MD}$ in the high-temperature range makes it clear that $d\lambda_1/dT < 0$ (see Table I). Therefore, further increase in the temperature in this temperature...
domain will reduce the relaxation rate (increase the relaxation time) as is observed. The relation \( k_T > k_M \) in this temperature range is also verified from the concentration derivative of \( \lambda_1 \) (in eq 12) for which experimental results give \( \delta \lambda_1/\delta [M] > 0 \) under the above conditions.

These arguments would in principle apply to even higher temperatures (room-temperature liquids for example), but the third term on the right-hand side of eq 5 eventually becomes dominant. Thus, the thermally activated process to the effective quenching channel \(~2500 \text{ cm}^{-1}\) above the zero-point level of \( ^1B_{2u} \) takes place at these elevated temperatures and eventually reduces the lifetime of the excited state. Again, this is in accord with the usual observations.

Although the possibility of the increasing lifetime of singlet benzene in small molecular liquids due to triplet-triplet annihilation cannot be completely ruled out from our experimental results, three other observations indicate that it is unlikely: (a) the fluorescence intensity is linear with input power over all powers and concentrations employed (less than 0.1-3 mJ/pulse) and \((\sim 2 \times 10^{-6} - \sim 2 \times 10^{-3} \text{ mol/L})\); (b) pyrazine triplet lifetime is 4 ms in \( \text{C}_2\text{H}_6 \) and \( \text{C}_6\text{H}_6 \) at 90 K and 50 \( \mu \text{s} \) at 150 K; and (c) naphthalene has been reported to have a 0.5-s triplet lifetime near room temperature in the liquid state. It is, therefore, rather unlikely that the singlet state can be repopulated via the triplet state to yield the increased lifetimes observed here above ca. 150 K. A somewhat more definitive experiment, adding \( \sim 6 \times 10^{-4} \text{ mol/L O}_2 \) to these solutions, shows an increase in fluorescence lifetime at high temperatures just as solutions without \( \text{O}_2 \). This further demonstrates that the monomer/excimer model is a reasonable approach to the description of the microkinetics of excited benzene in cryogenic liquid solutions for the duration of the fluorescence \((\sim 100 \text{ ns})\). The various rates shown in Table I indicate that the low-temperature and high-temperature limits are acceptable assumptions.

Finally, consider the results, presented in Figure 5, for the \( ^1B_{2u} \) fluorescence lifetimes in \( \text{C}_2\text{H}_6 \) and \( \text{C}_6\text{H}_6 \) as a function of temperature and concentration. Since these lifetimes are independent of concentration, the possibility of self-quenching can be ruled out as a dominant process. The temperature dependence of the lifetime in these solvents follows a thermal activation process with an activation energy close to the activation energy for diffusion. Two possible causes for such behavior can be considered: impurity quenching and intrinsic solvent triplet-state quenching of the \( ^1B_{2u} \) state.

For impurity quenching, the concentration of impurities would have to be 100 ppm for a unit probability of quenching upon diffusional encounters. An impurity concentration this high after numerous serial purification procedures seems quite unlikely. Moreover, two different solvents, \( \text{C}_2\text{H}_6 \) and \( \text{C}_6\text{H}_6 \), are involved, both of which yield the same concentration and temperature dependences for the \( ^1B_{2u} \) state. The experimental results for benzene and naphthalene\(^{14}\) (for which these are not unique solvents) further indicate that the quenching impurities in these systems must have singlet energy levels between the \( ^1B_{2u} \) state of benzene and the \( ^1B_{2u} \) state of naphthalene. Such impurities could account for the quenching of the benzene but not the naphthalene lifetime. Under these circumstances ketones and aldehydes of solventlike molecules might represent reasonable candidates for the quenchers. However, the purification procedures discussed in the Experimental Section should reduce the concentration of such species considerably in repeated steps.

Similar experiments with pyrazine\(^{14}\) reveal that \( ^3B_{3u} \) phosphorescence is quenched in \( \text{C}_2\text{H}_6 \), as well as in \( \text{C}_6\text{H}_6 \) and \( 1\text{-C}_6\text{H}_8 \) solvents, making it unlikely that impurities play a significant role in the overall excited-state kinetics, in general.

A rather more likely possibility is that the solvents themselves are responsible for the new \( ^1B_{2u} \) quenching mechanism in benzene/\( \text{C}_2\text{H}_6 \) and \( 1\text{-C}_6\text{H}_8 \) solutions. From electron-impact experiments\(^{16}\) it has been shown that \( \text{C}_2\text{H}_4, \text{C}_2\text{H}_6 \), and \( 1\text{-C}_6\text{H}_8 \) all have a triplet state at ca. 34 000 cm\(^{-1}\). The latter two triplet states could act as effective quenchers of the \( ^1B_{2u} \) state with a quenching probability of roughly \( 2 \times 10^{-3} \) per collision based on Figure 5 and viscosity data. Such a low quenching probability would be expected for singlet-triplet energy transfer. The much lower probability (see Figures 2–4) for \( \text{C}_2\text{H}_4/\text{C}_2\text{H}_6 \) quenching may be related to slight energy differences or size/geometry effects on the details of the collision process itself. On the other hand, the naphthalene \( ^1B_{2u} \) could not be trapped based on energy considerations and the pyrazine \( ^3B_{3u} \) could be trapped in the intersystem crossing process involving higher triplet states. Thus, while the question is certainly not settled, we do favor an intrinsic triplet-state solvent quenching mechanism for the \( ^1B_{2u} \) state of benzene in \( \text{C}_2\text{H}_6 \) and \( 1\text{-C}_6\text{H}_8 \) solvents.

Since the kinetic model for these results predicts that a number of pathways are involved in the relaxation process, one would expect nonexponential, or at least multieponential, experimental decays to arise. As indicated above, such behavior is not observed. Computer simulation of a single decay curve composed of two exponential components reveals that the observed total decay will be dominated by the major intensity contributor if both exponentials have the same order of magnitude decay constant. One on the other hand, if the decay rates are of different order of magnitude, the observed lifetime will be dominated by the component with the longer decay constant assuming they both contribute with the same intensity factor. The estimated rate constants presented in Table I indicate that at high temperature the observed lifetime will be mainly due to the monomer decay rate; at low temperatures the observed decay constant will also be determined by the monomer decay rate due to the low excimer population. At intermediate temperatures (including the turning point) the population of the excimer is smaller than the monomer and thus one still observes an apparent single exponential decay constant. Clearly, higher signal-to-noise ratio, especially at long times, should reveal multieponential behavior. Thus, this model seems to be capable of addressing the experimental observations qualitatively; a quantitative theoretical fit proves not useful here because too many adjustable parameters are available in the rate equations and too few experimental component rate constants are observable.

Summary and Conclusions

The fluorescence lifetime of the \( ^1B_{2u} \) state of benzene has been investigated in cryogenic solvents. The observed anomalous temperature dependence of this lifetime in \( \text{C}_2\text{H}_6, \text{C}_6\text{H}_6 \), and \( \text{C}_6\text{H}_8 \) solvents is attributed to the formation at low temperature and dissociation at higher temperature of benzene excimers. The effective cage structure of the local environment within the solvent provides for isolation of the excited monomers but, as diffusion brings local cages together with two monomers

Spectroscopic Studies of Pyrazine in Cryogenic Solutions

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The first excited singlet ($^{1}B_{2u}$) and triplet ($^{3}B_{3u}$) states of pyrazine are studied in the cryogenic liquids CH₄, C₂H₆, C₃H₈, C₄H₁₀, C₂H₄, C₃H₆, and 1-C₄H₈. The reported data include $^{1}B_{2u} \rightarrow ^{1}A_{2u}$ absorption, fluorescence, and lifetimes and $^{3}B_{3u} \rightarrow ^{1}A_{2u}$ phosphorescence and lifetimes as a function of temperature and concentration. From the behavior of the $^{1}B_{2u} \rightarrow ^{1}A_{2u}$ system it is concluded that hydrogen bonding is an important feature of the intermolecular potential in these solutions. The lifetime of the singlet state is quite short with an upper limit of ~5 ns. The $^{3}B_{3u} \rightarrow ^{1}A_{2u}$ phosphorescence has a measured 4-ms lifetime at 90 K which is consistent with an impurity quenching mechanism and impurity concentration of 0.01 ppm. It has been possible to separate out radiative, nonradiative, and impurity quenching rate constants in these systems for the $^{3}B_{3u}$ state of pyrazine. An activation energy for the temperature-dependent radiationless process of ~2 kcal/mol is regarded as the hydrogen-bonding energy between solvent and pyrazine (N-HC) in the excited $^{3}B_{3u}$ state.

I. Introduction

Relaxation times and absorption and emission spectra have been demonstrated to yield important new information concerning the properties and structure of cryogenic liquids. The observed Franck-Condon shifts between the absorption and emission origins and temperature-dependent low-energy tails of the main features in the emission spectrum of C₆H₆ and C₅H₈ systems have provided new insights into the intermolecular interactions between solute and solvent molecules. These effects can be understood on the basis of the known qualitative behavior of the polarizabilities of aromatic systems. The fluorescence lifetimes of these systems have been shown to be roughly the same as those observed in very dilute gases (i.e. ~150 ns for C₆H₆ and ~250 ns for C₅H₈). The phosphorescence of these molecules has yet to be observed in cryogenic liquids, most likely due to a lack of solvent purity. (For a 1-s lifetime to be realized, an O₂-like quencher must not be present at concentrations greater than 10⁻⁵ ppm.)

Unlike the previously mentioned systems, the pyrazine molecule undergoes nπ* transitions upon excitation to its first excited singlet ($^{1}B_{2u}$) and first excited triplet ($^{3}B_{3u}$) states. Consequently, the excited-state pyrazine system represents a different possible probe of the intermolecular interactions, structure, and dynamics of cryogenic solutions. The spectroscopic properties of pyrazine are now well established for gas and solid phases. A careful comparison and correlation of the spectroscopic data for pyrazine in all three states of matter can now be made. The results of such studies discussed in this report indicate that hydrogen bonding (N-HC) and diffusion-controlled impurity quenching processes play an important role in cryogenic solutions (CH₄, C₂H₆, C₃H₈, C₄H₁₀, C₂H₄, C₃H₆, and 1-C₄H₈). The hydrogen-bonding strength, phosphorescence lifetime for pyrazine as a function of temperature, and a limit to the impurity concentration in these solvents can be measured.

II. Experimental Section

The general preparation and purification procedures for the solvents and solute have been discussed in the previous reports. So that the phosphorescence lifetime of the long-lived triplet state of pyrazine can be measured, highly...