

Spectroscopy of Naphthalene in Simple Molecular Liquids

F. Li, J. Lee, and E. R. Bernstein*

Department of Chemistry and Condensed Matter Sciences Laboratory, Colorado State University, Fort Collins, Colorado 80523
(Received: October 4, 1982; In Final Form: November 18, 1982)

Optical spectra of the first excited singlet state ($^1B_{3u}$) of naphthalene in cryogenic molecular hydrocarbon alkane and alkene liquids (CH_4 , C_2H_4 , C_2H_6 , C_3H_6 , C_3H_8 , $1-C_4H_8$) have been obtained and are discussed in terms of the solute-solvent intermolecular interaction. Data include gas-to-liquid shifts, Franck-Condon shifts, line widths for absorption and emission, and their temperature dependences. Naphthalene line widths and their temperature dependences and Franck-Condon shifts are smaller than those found for benzene but the gas-to-liquid shifts for both systems are quite similar. Based on these results and the comparison with similar benzene data, the ground- and excited-state Lennard-Jones type potential curves for naphthalene-solvent interactions can be generated. The main conclusions are that naphthalene has a stronger interaction with the solvent than does benzene, the interaction scales with solvent polarizability, and the change in cavity radius upon excitation is greater for benzene than for naphthalene. Lifetime data have also been obtained for the naphthalene fluorescence. At low temperature, the liquid-state lifetime for fluorescence is roughly the same as that found in the low-pressure gas (~ 300 ns). A small temperature dependence is characterized for these low-concentration solutions leading to an activation energy for naphthalene collision-induced intersystem crossing of ~ 100 cm $^{-1}$. The excimer formation and monomer regeneration mechanism reported for benzene is also observed in naphthalene C_3H_6 and C_3H_8 solutions but it is of much less importance to the overall kinetics.

Introduction

Spectroscopic and lifetime studies of probe molecules in cryogenic small-molecule liquid solvents have been demonstrated to yield useful information concerning the microstructure and microdynamics of the liquid state.¹⁻³ Electronic absorption and emission data include gas-to-liquid shifts, Franck-Condon shifts, line widths, and their temperature dependences. These results can be employed in conjunction with calculations to study the intermolecular solvent/solute potential surface near its equilibrium separation distance. The fluorescence lifetimes trace the fate of solute molecules in the liquid at low concentration. Comparing these with the lifetimes of molecules in the low-pressure gas phase and in room-temperature liquids, one can extract information on the radiationless transitions in the condensed phase. In addition, some qualitative understanding of long-time (tens of nanoseconds) solvent cage dynamics can arise from such investigations.

In this paper we report the absorption and emission data for the first excited singlet state ($^1B_{3u}$) of naphthalene in cryogenic hydrocarbon liquids. These data are analyzed through comparison with those obtained for benzene in the same solvent and, consequently, information on the naphthalene/solvent intermolecular potential is generated. Model potential calculations can be fitted to these data on the basis of a Lennard-Jones formulation. It is suggested that the ground-state solute-solvent interaction is stronger for naphthalene than for benzene in the same solvent. The excited-state potential is also deeper for naphthalene than for benzene. However, such a simple potential model fails to represent the line width behavior.

The lifetime of the naphthalene $^1B_{3u}$ state fluorescence in various cryogenic liquids is also reported. The results are consistent with a model in which the (isoenergetic) intersystem crossing from the zero-point levels of the $^1B_{3u}$ state to the lowest triplet state ($^3B_{2u}$) of naphthalene is saturated due to the dense set of vibronic triplet states.

Thus, for this pathway the radiationless relaxation is temperature (solvent collision) independent. However, collisions may induce intersystem crossing to the much less dense manifold of high triplet states. The formation of naphthalene excimers is less probable than the formation of benzene excimers; this observation is rationalized on the basis of solvent-solute interactions, monomer shape, and monomer diffusion.

Experimental Section

Sample preparation and instrumental techniques have been described in other papers from our laboratory.^{1,3,4} It has been found that impurities such as β -methyl-naphthalene can cause difficulties with fluorescence spectra⁵ and lifetime studies especially in the crystal. Consequently, potassium treatment of the naphthalene (Fisher Gold Label) was employed to reduce the level of such contaminants.⁶ Although zone refining is a further step that helps remove impurities such as anthracene,⁷ this procedure was omitted because it was felt unnecessary in these experiments. The naphthalene was further purified by vacuum sublimation following the potassium treatment. Since naphthalene has a low vapor pressure and a high melting temperature, the deposition process is somewhat revised compared to that which has been previously described. A 150-mL stainless-steel bottle was added to the manifold, filled with $C_{10}H_8$ vapor and kept at $\sim 10^\circ C$ higher than the temperature of the naphthalene sample. Solvent was then passed through this chamber in the deposition process. The actual concentrations thus generated are very close to the calculated values expected on the basis of vapor pressure ratios and oscillator strength.

Results

The absorption and emission spectra of the first excited singlet state of naphthalene have been obtained in CH_4 ,

(1) F. Li, J. Lee, and E. R. Bernstein, *J. Phys. Chem.*, **86**, 3606 (1982).

(2) G. W. Robinson, R. A. Auerbach, and J. A. Synowiec, *Chem. Phys. Lett.*, **82**, 219 (1981).

(3) F. Li, J. Lee, and E. R. Bernstein, *J. Phys. Chem.*, **87**, 254 (1983).

(4) E. R. Bernstein and J. Lee, *J. Chem. Phys.*, **74**, 3159 (1981).

(5) H. C. Wolf, *Adv. At. Mol. Phys.*, **3**, 119 (1967).

(6) D. M. Hanson and G. W. Robinson, *J. Chem. Phys.*, **43**, 4174 (1965).

(7) S. T. Gentry and R. Kopelman, private communication.

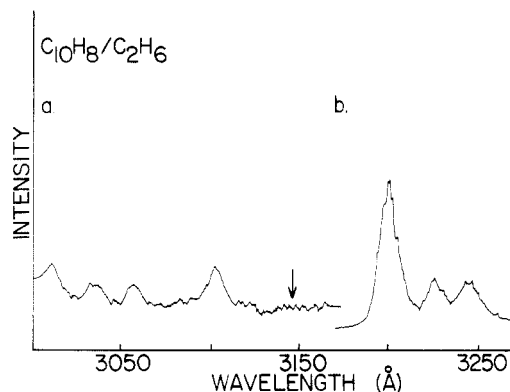


Figure 1. Absorption (a) and emission (b) spectra of the first excited singlet state $^1B_{3u}$ of naphthalene (5 ppm) in liquid C_2H_6 at 90 K. The assignment of the features is as follows: $\bar{8}_0^1$ at 3100 Å, $\bar{7}_0^1$ and $\bar{8}_0^1 9_0^1$ at 3060 Å, $\bar{8}_0^1 8_0^1$ and 6_0^1 at 3035 Å, $\bar{8}_0^1 7_0^1$, 4_0^1 at 3115 Å, 8_0^1 at 3200 Å, and $\bar{8}_0^1$ at 3225 Å. The arrow indicates the 0_0^0 at 3147 Å. The notation for the modes (barred and unbarred, ref 19) represents b_{1g} and a_g vibrational symmetry, respectively.

TABLE I: Absorption and Emission Line Widths^a of Naphthalene and Benzene in Various Solvents

solvent	temp, K	absorption line width, cm^{-1}
Naphthalene		
C_2H_6	150	142
C_2H_4	165	149
C_3H_8	150	142
Benzene		
C_2H_6	150	190
C_2H_4	165	208
C_3H_8	150	190
solvent	temp, K	emission line width, cm^{-1}
Naphthalene		
C_2H_6	90	110
	150	146
	180	183
C_2H_4	110	146
C_3H_8	90	140
	150	182
Benzene		
C_2H_6	90	172
	150	245
	180	331
C_2H_4	110	238
C_3H_8	90	227
	150	300

^a In cm^{-1} ; error $\pm 20 cm^{-1}$.

C_2H_4 , C_2H_6 , C_3H_8 , C_3H_6 , and $1-C_4H_8$. Figure 1 shows the spectra of 5 ppm naphthalene in C_2H_6 at 90 K. Assignment of features in the absorption is made through comparison with data from the molecular-jet experiment.⁸ The assignment of the emission features is consistent with that of Hollas.⁹ Table I gives the absorption and emission line widths of naphthalene in various solvents at the same temperature. Also shown in Table I are the absorption and emission line widths of benzene for comparison. It is clear from Table I that the absorption and emission line widths of naphthalene in all solvents studied are narrower than those found for benzene under the same conditions. The gas-to-liquid shifts for naphthalene are listed in Table II along with the Franck-Condon shifts for the various solvents. The values for benzene are also included in Table

TABLE II: Gas-to-Liquid Shifts^a in Absorption and Franck-Condon Shifts^a for Naphthalenes and Benzene in Various Solvents

	naphthalene		benzene		$\frac{\Delta_{FC}^-(benzene)}{\Delta_{FC}^-(naphthalene)}$
	Δ_{gl}^b	Δ_{FC}	Δ_{gl}^c	Δ_{FC}	
CH_4	-220		-171	32	
C_2H_6	248	28	247	58	(2.1)
C_2H_4	260	38	270	69	(1.8)
C_2H_2	274	43	253	96	(2.2)
C_3H_6	300	49	279	119	(2.4)
$1-C_4H_8$	288	61	303	124	(2.0)

^a In cm^{-1} ; uncertainty $\pm 20 cm^{-1}$. ^b Naphthalene gas-phase 0_0^0 absorption at $32\,020 cm^{-1}$, D. P. Craig, J. M. Hollas, M. F. Redies, and S. C. Wait, *Trans. R. Soc. London, Ser. A*, 253, 543 (1961). Value in parentheses has $\pm 40 cm^{-1}$ uncertainty. ^c Benzene gas-phase 0_0^0 absorption at $38\,289 cm^{-1}$; ref 20.

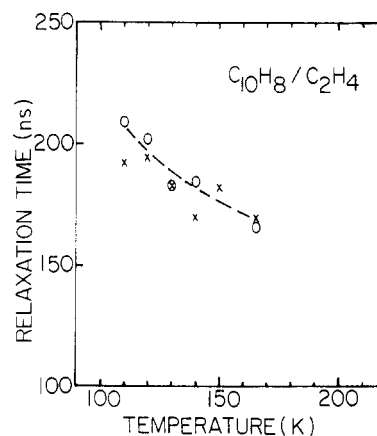


Figure 2. Lifetime of naphthalene $^1B_{3u}$ state as a function of temperature in liquid C_2H_4 : (X) 0.1 and (O) 1 ppm. (1 ppm = 1.37×10^{-5} mol/L.)

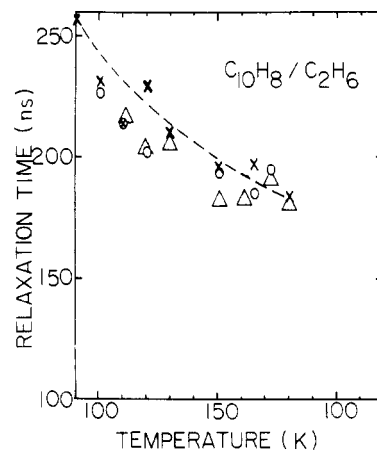


Figure 3. Lifetime of naphthalene $^1B_{3u}$ state as a function of temperature in liquid C_2H_6 : (X) 0.1, (O) 0.5, and (Δ) 3.5 ppm. (1 ppm = 1.9×10^{-5} mol/L.)

II for comparison. It is found that, while the gas-to-liquid shifts for naphthalene and benzene are quite comparable, the Franck-Condon shifts for naphthalene are smaller by a factor of 2 than those of benzene.

A study of the lifetime of naphthalene in these solvents as a function of temperature and concentration has been performed and the results are given in Figures 2–6. The relatively low solubility of naphthalene in these solvents prevents the study of high concentrations (greater than 20 ppm). Except in C_3H_6 and C_3H_8 solvents, it is found that a change in concentration from 0.1 to 10 ppm does

(8) S. M. Beck, D. E. Powers, J. B. Hopkins, and R. E. Smalley, *J. Chem. Phys.*, 73, 2019 (1980).

(9) J. M. Hollas, *J. Mol. Spectrosc.*, 9, 138 (1962).

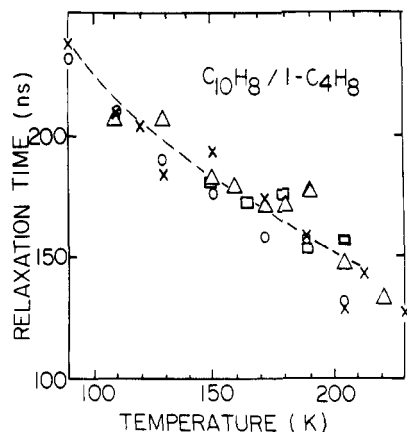


Figure 4. Lifetime of naphthalene $^1B_{3u}$ state as a function of temperature in liquid 1-C₄H₈: (X) 0.1, (O) 0.2, (Δ) 1, and (\square) 7 ppm. (1 ppm = 1.06×10^{-5} mol/L.)

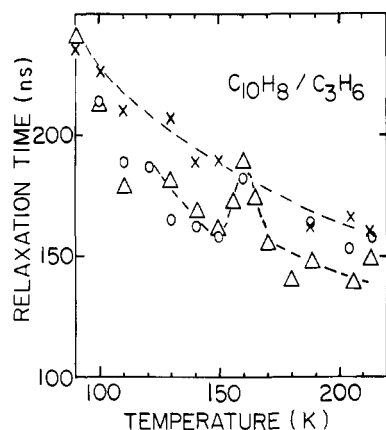


Figure 5. Lifetime of naphthalene $^1B_{3u}$ state as a function of temperature in liquid C₃H₆: (X) 0.1, (O) 1, and (Δ) 5 ppm. A small increase of lifetime has been observed as temperature increases. At even higher temperatures, the reduction of lifetime indicates an increase in the competing decay rate from nonradiative process. (1 ppm = 1.23×10^{-5} mol/L.)

not result in a noticeable reduction of the lifetime. In C₃H₆ and C₃H₈ solvents, however, due to the large liquid temperature ranges obtainable and low viscosity of these solvents, a small but consistently reproducible increase in the lifetime at high temperature can be observed as shown in Figures 5 and 6. This is likely due to the breakup of a small population of excimers at these higher temperatures. Note, however, that the regeneration of monomers from the excimer typically occurs near 150–170 K, indicating that solvent behavior may play a fundamental role in this overall kinetic process.^{1,2}

Discussion

The spectroscopic data for naphthalene in cryogenic hydrocarbon liquids show the same main features observed for benzene: nearly temperature-independent absorption line widths, emission line widths which broaden to the low-energy side as temperature is increased, a low-temperature, low-concentration lifetime approaching that found in the low-pressure gas phase, and a gradual increase in the (unimolecular) nonradiative rate as temperature is increased. As in the case of benzene, the naphthalene data could be used to obtain information on the reduced ground-state potential surface by applying McRae's formula¹⁰ and making various approximations, assuming all the appropriate oscillator strengths and frequencies are

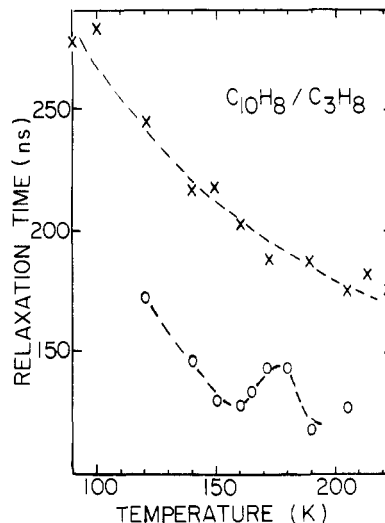


Figure 6. Lifetime of naphthalene $^1B_{3u}$ state as a function of temperature in liquid C₃H₈: (X) 0.1 and (O) 1 ppm. The small values of lifetime are due to a small concentration of impurities in the solvent. Nevertheless, the small increase of lifetime observed at ca. 170 K is the result of the breakup of excimer at these higher temperatures. (1 ppm = 1.33×10^{-5} mol/L.)

known. Even the benzene analysis, however, required a base or standard solution (cyclohexane) upon which to set parameters.¹ Since the trends and general features of the naphthalene and benzene data sets are so similar, benzene actually serves as a more realistic and reliable model system than even the calculations.

On the other hand, the naphthalene excited-state kinetics seem more temperature and concentration independent over the ranges followed in these studies. This indicates that the self-quenching mechanism, so central to the benzene solution kinetics, is less of a factor of naphthalene. Thus, the solution kinetics in the ensuing discussion will not be dealt with in a fashion parallel to that already presented for benzene.³

Intermolecular Potentials. As shown for benzene,¹ solute molecular spectra can be usefully employed in the study of solute-solvent intermolecular interactions and potentials. For the sake of clarity and comparison, the benzene data and analysis procedure will be reviewed. In absorption, the vertical Franck-Condon process projects the ground-state equilibrium position (for a given temperature) onto the excited-state intermolecular potential surface. Liquid-state emission spectra, on the other hand, probe the corresponding part of the ground-state intermolecular potential from the excited-state equilibrium configuration (for a given temperature). Since it is likely that the intermolecular potential consists of a steep repulsive part and a relatively flat long-range attractive part,¹¹ the data for both the naphthalene and benzene systems require an excited-state solvent/solute cage that is smaller than the ground-state one. One then approximates the difference between the ground- and excited-state potential minima in the liquid as the absorption 0_0^0 transition energy. The (typically negative) gas-to-liquid shift is obtained by subtracting this value from the gas-phase 0_0^0 transition energy. Under these assumptions, the difference between the absorption and emission gas-to-liquid shifts, that is, the Franck-Condon shift, can be regarded as the energy difference between the ground-state potential minimum and the ground-state potential energy vertically projected from the potential minimum of the excited-state

(10) E. R. McRae, *J. Phys. Chem.*, **61**, 562 (1957).

(11) R. O. Watts and I. J. McGee, "Liquid State Chemical Physics", Wiley, New York, 1976.

intermolecular potential. The Franck-Condon shifts in this approximate analysis for benzene thus are assumed to contain information on the repulsive part of the ground-state intermolecular potential.

In the previous benzene analysis,¹ an identical form for the reduced ground-state intermolecular coordinate was assumed for all solvents and a standard solvent, namely, cyclohexane, with an averaged intermolecular distance for the ground-state potential minimum of 3 Å, was employed to calculate the potential as a function of cavity size and percent of change in cavity size upon excitation.¹⁰

Since not all the transition frequencies and oscillator strengths are known for naphthalene, a similar calculation would not be very reliable. However, not only is the comparison between naphthalene and benzene reliable, it is also useful, physically meaningful, and capable of generating a qualitative picture of the intermolecular interactions at least to some extent.

For the sake of comparison, consider that the intermolecular interactions can be modeled by a simple Lennard-Jones potential written in the following form for the ground (') and excited (') states:

$$E''(r) = 4\epsilon''[(\sigma''/r)^{12} - (\sigma''/r)^6] \quad (1)$$

$$E'(r) = 4\epsilon'[(\sigma'/r)^{12} - (\sigma'/r)^6] + E_0 \quad (2)$$

While, as we show, the powers 12-6 are not central to this analysis, the general form of the potential is; a more complicated three- or four-parameter potential would not be usable with the data. In eq 1 and 2, ϵ and σ are parameters for the well depth and the equilibrium position, respectively. Since, upon excitation, well depth and position are expected to change, it is assumed that $\sigma' \neq \sigma''$ and $\epsilon' \neq \epsilon''$. Consequently, the model begins with two equations and six unknowns. The absorption and emission data provide that

$$E'(r''_{\min}) - E''(r''_{\min}) = E_{\text{abs}} \quad (3)$$

$$E'(r'_{\min}) - E''(r'_{\min}) = E_{\text{em}} \quad (4)$$

in which E_{abs} and E_{em} are the observed absorption and emission 0₀ frequencies of the solute in the liquid and r''_{\min} and r'_{\min} are the minimum potential (equilibrium) positions of the ground and excited states, respectively. If the ratio of well depths is also taken as $\gamma = \sigma'/\sigma''$, eq 1-4 can be combined to give

$$(\gamma^{12} - 2\gamma^6)\epsilon' + \epsilon'' = \Delta_{\text{gl}} \quad (5)$$

$$\epsilon' + [(1/\gamma)^6]\epsilon'' = \Delta_{\text{FC}} - \Delta_{\text{gl}} \quad (6)$$

in which Δ_{gl} is the gas-to-liquid shift and Δ_{FC} is the Franck-Condon shift. In order to solve these equations one needs to make further assumptions involving γ . First, $\gamma \leq 1$, that is, the excited-state molecule interacts more strongly with the solvent cage than does the ground-state molecule. This relation has been determined for C_6H_6 (C_6D_6),¹ $\text{C}_4\text{N}_2\text{H}_2$,¹² and C_7H_8 .¹³ Second, $\epsilon_{\text{solvent}} \leq \epsilon' \leq \epsilon_{\text{solute}}$; that is, the energy parameter for the ground-state Lennard-Jones interaction potential between two different molecules (solute and solvent) is assumed to have a value between the values of the solute-solute and solvent-solvent parameters, ϵ_{solute} and $\epsilon_{\text{solvent}}$. One can use the first assumption to generate a series of ϵ' and ϵ'' and employ the second assumption to confine the range of γ to an

"appropriate" value. Thereby, specific potentials can be simultaneously constructed for the ground and excited states.

Application of the above approximate scheme to the $\text{C}_{10}\text{H}_8/\text{C}_3\text{H}_8$ and $\text{C}_6\text{D}_6/\text{C}_3\text{H}_8$ systems results in a range of γ for each system. Although there is a region of energy for which $\epsilon''_{\text{C}_{10}\text{H}_8}$ and $\epsilon''_{\text{C}_6\text{D}_6}$ overlap each other, the cavity size ratio γ does not overlap and gives a larger value for $\text{C}_{10}\text{H}_8/\text{C}_3\text{H}_8$ than $\text{C}_6\text{D}_6/\text{C}_3\text{H}_8$. Thus, upon excitation the model predicts that the change in cavity size for C_{10}H_8 is smaller than for C_6D_6 in the propane solvent. This interesting result can be correlated with the polarizability data for C_6D_6 and C_{10}H_8 . According to the previous benzene results¹ and recent observations for the toluene system,¹³ the solute-solvent interaction scales quite accurately with the solvent and solute polarizability and is independent of their dipole moment. The ratio of the excited- to ground-state polarizability (α'/α'') for these two solute molecules indicates a smaller value for C_{10}H_8 (~ 1.14)¹⁴ than for C_6D_6 (~ 1.2);¹⁵ hence, $\gamma_{\text{C}_{10}\text{H}_8} > \gamma_{\text{C}_6\text{D}_6}$. The smaller spectral line width for C_{10}H_8 in comparison to C_6D_6 , which is evident in all solvents (Table I), also supports a smaller cavity change upon C_{10}H_8 excitation.

In order to compare the intermolecular interaction for C_{10}H_8 and C_6D_6 solvent systems, one must select a set of ($\gamma, \epsilon', \epsilon''$) for each system. As an example, the middle value for each bracket is picked for ϵ'' . Although this is a rather arbitrary choice, data sets thus generated are well fitted to the above polarizability argument; that is, a large polarizability corresponds to a large interaction potential energy minimum (ϵ), and a small energy increment ($(\epsilon' - \epsilon'')/\epsilon''$) corresponds to a small polarizability increment ($(\alpha' - \alpha'')/\alpha''$) for C_{10}H_8 . Once ϵ'' and ϵ' are decided, the Franck-Condon shifts for the individual ground- and excited-state wells can be determined.

As a consequence of these Lennard-Jones potentials, the molecular excited state has a larger Franck-Condon shift than the ground state, a result which is at variance with the previous benzene-analysis assumption. This is a direct consequence of the larger γ values and relatively small values for ϵ' and ϵ'' in the Lennard-Jones potential model. If the intermolecular potential were truly of this form for both states (as will be shown below, it must not be, however), the previous potential well for C_6D_6 in cryogenic liquids¹ should reflect the attractive part of the excited state rather than the repulsive part of the ground state.

Similar comparison between C_6D_6 and C_{10}H_8 in solvents other than C_3H_8 further support the polarizability-dependent trends and larger excited-state Franck-Condon shifts than ground-state ones. Moreover, the cavity ratio γ ($=\sigma'/\sigma''$) for C_{10}H_8 (or C_6D_6) in various solvents is found to scale with polarizability. As solvent polarizability increases, the solvent cavity becomes smaller upon excitation (smaller γ) in agreement with the previous ab initio calculation for C_6D_6 .¹ However, the absolute ratio γ is larger for the Lennard-Jones model than for the ab initio one and the Lennard-Jones model is also more sensitive to changes in cavity size and solvent polarizability. The reasons for this lie in a steep r dependence and relatively shallow ϵ' and ϵ'' for the Lennard-Jones potentials.

The Lennard-Jones model approach has two advantages: comparison between many different systems is possible as it serves to organize a good deal of data; and it can provide some insight, in principle, into the molecular excited-state interactions.

(12) J. Lee, F. Li, and E. R. Bernstein, *J. Phys. Chem.*, **87**, 260 (1983).

(13) J. Lee, F. Li, and E. R. Bernstein, *J. Phys. Chem.*, following article in this issue.

(14) H. Meyer, K. W. Schulte, and A. Schweig, *Chem. Phys. Lett.*, **31**, 187 (1975).

(15) R. Mathies and J. C. Albercht, *J. Chem. Phys.*, **60**, 2500 (1974).

TABLE III: Decay Rate of Naphthalene and Benzene in Various Solvents^a

	<i>a</i>	<i>b</i>	ΔE , cm ⁻¹
Naphthalene			
C ₂ H ₆	2.7×10^6	6.2×10^6	104
C ₃ H ₈	2.6×10^6	6.8×10^6	95
1-C ₄ H ₈	3.0×10^6	7.2×10^6	114
Benzene			
C ₂ H ₆ (1 ppm)	5.3×10^6	1.5×10^7	215
(0.3 ppm)	4.2×10^6	3.8×10^6	57
C ₃ H ₈ (1 ppm)	6.5×10^6	2.0×10^7	184
(0.3 ppm)	4.7×10^6	7.1×10^6	86

$$^a k = a + be(\Delta E/k_B T).$$

There are, however, two serious problems with the Lennard-Jones approach. First, it fails to predict the proper spectroscopic line widths based on a simple Boltzmann population in the ground- and excited-state wells. According to the Lennard-Jones model the emission lines should be broader than the absorption lines; the opposite is observed. Second, the absorption lines are predicted to be temperature dependent but not the emission features. These two failures are quite important as they suggest that the shapes and relative depths of the two wells are incorrectly modeled.

These two contradictions suggest that the restrictions of well depth ($\epsilon''_{\text{solute}} \geq \epsilon'' \geq \epsilon''_{\text{solvent}}$) and shape (12-6 powers) should be released. For simplicity the 12-6 power restriction was relaxed for the molecular excited state, which modifies eq 2 in the following manner:

$$E' = \{[m/n]^{n/(n-m)} - [m/n]^{m/(n-m)}\}^{-1} \epsilon'[(\sigma'/r)^n - (\sigma'/r)^m] + E_0 \quad (7)$$

in which *n* and *m* are the powers for the repulsive and attractive parts of the potential, respectively.

Several *n-m* pairs, including 12-1, 12-3, 24-3, 10-4, 9-3, and 6-1, have been tested at different potential energies. The results show that none of these pairs satisfies the line width value and its temperature response simultaneously, although all other experimental observations can be well fitted. Such a disagreement between calculated and observed results suggests that a more complicated intermolecular interaction than a simple two-parameter Lennard-Jones type is required for these liquids. More complicated three-parameter potentials, however, would not be useful in data comparison and organization.

This Lennard-Jones approach is useful in comparing data for different systems but only presents part of the overall interaction picture.

Lifetimes. The study of naphthalene lifetimes in cryogenic liquids shows that at low temperature (*T* < 100 K) the observed lifetimes approach those of the dilute low-pressure gas-phase value. This indicates that the quantum yields for fluorescence in these two quite different environments are almost the same. Collisions between naphthalene and the surrounding solvent cage molecules must be weak and ineffective in enhancing intersystem crossing. Two factors contribute to this observation: low kinetic energy of the solvent molecules generating a more rigid solvation cage structure and a dense triplet vibronic manifold from the lowest triplet state (³B_{2u}) at the ¹B_{3u} energy. Benzene behaves in a comparable fashion once the kinetics are extrapolated to infinite dilution to suppress the excimer formation-monomer regeneration mechanism. Table III contains these comparative results.

The decay rate for naphthalene as a function of temperature in 1-C₄H₈ can be written as

$$k = 3.0 \times 10^6 + (7.2 \times 10^6) \exp(-114/KT) \quad (8)$$

The temperature-independent part of eq 8 yields a lifetime of ~300 ns, which is close to the reported lifetime in the gas phase.¹⁶ The second term can be attributed to collisionally induced intersystem crossing.¹⁷ The activation energy associated with this term (~100 cm⁻¹) is roughly twice as large as that found for benzene. The temperature-independent part of the benzene decay rate in very dilute solutions is also consistent with the gas-phase collision-free lifetime (~200 ns, C₆D₆; ~100 ns, C₆H₆).¹⁸ This discussion suggests that the temperature-independent part of both decay rates is governed by an intramolecular relaxation process and that the temperature-dependent part is governed by collisionally induced intersystem crossing. This latter effect increases with temperature and is more important for naphthalene than benzene as indicated by the activation energies.

It is known that the energy difference between the first excited singlet state and the lowest triplet state of naphthalene is ~10000 cm⁻¹,¹⁹ this difference for benzene²⁰ is ~8600 cm⁻¹. Thus, a dense set of lowest triplet vibronic states can be expected to be isoenergetic with the first excited singlet states of these systems. The dense triplet manifolds drive the irreversible nonradiative processes in the collision-free single molecule (large-molecule limit). In low-temperature liquids, weak collisions with the solvent molecules do not increase the coupling between these two electronic states; that is, fluorescence quenching through this channel has been saturated.²¹ However, the higher energy triplet states do not have a dense manifold of states isoenergetic with the first excited singlet state zero-point level. This circumstance, of course, corresponds to the small-molecule limit.²² In this situation, collisions with the surrounding solvent-shell molecules can move the less dense manifold of upper triplet states into and out of resonance with the lowest singlet state zero-point level and thus alter the nonradiative intersystem crossing rates. One predicts that the smaller the singlet-triplet separation is, the larger the activation energy associated with this process will be.¹⁷ It is found that the energy difference between the first excited singlet state and the next lowest triplet state is ~300 cm⁻¹ for naphthalene (32020 (¹B_{3u}) - 31700 (³B_{3u}) cm⁻¹)¹⁹ and ~1650 cm⁻¹ for benzene (38289 (¹B_{2u}) - 36650 (³E_{1u}) cm⁻¹).²⁰ Therefore, the activation energy for collisionally induced intersystem crossing is expected to be larger for naphthalene than for benzene, as is observed.

The concentration independence of the lifetime of naphthalene in cryogenic solvents would indicate a non-dominant excimer formation decay rate. There are two possible general explanations for this observation. First, the just-discussed large activation energy (~100 cm⁻¹) for intersystem crossing implies a large change in lifetime as the temperature is increased. Thus, naphthalene intersystem crossing could actively compete with the nonradiative rate due to excimer formation. Secondly, the probability of excimer formation for naphthalene solutions may simply be smaller than for benzene solutions. There

(16) N. Ohta and H. Baba, *J. Chem. Phys.*, **76**, 1654 (1982).

(17) R. G. Bennett and P. J. McCartin, *J. Phys. Chem.*, **44**, 1969 (1966).

(18) A. S. Abramson, K. G. Spears, and S. A. Rice, *J. Chem. Phys.*, **56**, 2291 (1972).

(19) M. Stockburger, H. Gattermann, and W. Klusmann, *J. Chem. Phys.*, **63**, 4529 (1975).

(20) C. S. Parmenter, *Adv. Chem. Phys.*, **22**, 365 (1972).

(21) K. F. Freed, *Adv. Chem. Phys.*, **42**, 207 (1980).

(22) (a) B. K. Selinger, *Aust. J. Chem.*, **19**, 825 (1966); (b) J. B. Aladekomo and J. B. Birks, *Proc. R. Soc. London, Ser. A*, **284**, 551 (1965); (c) N. Matagu, M. Tomura, and H. Hishimura, *Mol. Phys.*, **9**, 367 (1965).

are several factors that can contribute to the overall probability of excimer formation. The larger size of naphthalene may mean slower diffusion in solution although the long lifetime could compensate for this. There are also fewer ways to form a naphthalene excimer than a benzene excimer. Energetics could also be a factor for the probability of excimer formation. Since naphthalene has a stronger interaction with the solvent than does benzene, the naphthalene-solvent cage is more stable and this may affect excimer formation; the collisional cross section for excimer formation thus becomes smaller and the excimer may have a shorter lifetime.

Nonetheless, a small but consistently reproducible increase in the lifetime of naphthalene in C_3H_8 and C_3H_6 solvents around 150–170 K, as shown in Figures 5 and 6, indicates some formation of excimers. These particular solvents show the effect due to their wide liquid-state range as a function of temperature and low viscosity. The qualitative behavior in these systems is quite similar to that found for benzene.

Finally, an extrapolation of the lifetime of naphthalene from low temperature to room temperature yields a value of ~ 140 ns at ~ 300 K. This is higher than the usually reported lifetime for naphthalene fluorescence at room temperature (120 ns).²² The lower room-temperature measured value can be attributed to a sudden increase of the intersystem crossing rate at an excess singlet-state energy of 1000 cm^{-1} .¹⁶ The same situation was found for benzene for which the anomaly appears at $\sim 2500\text{ cm}^{-1}$ above the vibrationless level of the $^1B_{2u}$ state.²⁰

Summary and Conclusions

Spectroscopic data for naphthalene in cryogenic hydrocarbon solutions have been analyzed and compared to those data obtained from benzene. The smaller naphthalene Franck-Condon shifts and line widths suggest that upon excitation the solute-solvent intermolecular interaction changes less in the case of naphthalene solutions than in the case of benzene solutions. On the other hand, the naphthalene-solvent interaction is stronger in both states than the benzene-solvent interaction. This trend scales well with solvent and solute polarizabilities. The Lennard-Jones model used to extract these ideas, however, does not predict the proper line widths or their temperature dependences. Thus, while useful, the Lennard-Jones type potential is not quantitatively correct for these systems.

Lifetime data show that, in low-temperature liquids, naphthalene has a fluorescence decay rate close to the value for the isolated free molecule; this is also true for benzene. An analysis of the lifetime of these two systems indicates that the temperature dependence of the decay rate is due to collisionally induced intersystem crossing to the next lower triplet state.

Acknowledgment. This work was supported in part by the NSF and the ONR.

Registry No. CH_4 , 74-82-8; C_2H_4 , 74-85-1; C_2H_6 , 74-84-0; C_3H_6 , 115-07-1; C_3H_8 , 74-98-6; 1- C_4H_8 , 106-98-9; naphthalene, 91-20-3; benzene, 71-43-2.

Spectroscopic Studies of Toluene in Simple Molecular Liquids

J. Lee, F. Li, and E. R. Bernstein*

Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523 (Received: September 23, 1982)

Absorption and emission spectra and fluorescence lifetimes are reported for the 1B_1 state of toluene in a number of simple hydrocarbon solvents (CH_4 , C_2H_6 , C_3H_8 , C_2H_4 , C_3H_6 , and 1- C_4H_8). Spectroscopic data such as gas-to-liquid shifts, intermolecular Franck-Condon shifts, line widths, and their temperature dependences can be employed to study potentials present in the cryogenic liquid near the equilibrium separation for solvent and solute. Lifetimes as a function of concentration and temperature indicate that toluene excimers do not form, apparently due to steric hindrance. The results for toluene are compared and contrasted to those for benzene. The intermolecular interactions are nearly identical for the two systems, suggesting that polarizabilities and not dipole moments are important for C_nH_m solvents and hydrocarbon probe systems. Toluene relaxation kinetics and their temperature dependences are discussed.

Introduction

Optical spectroscopic studies of aromatic probe systems (C_6D_6 ,¹ $C_4H_2N_4$,² $C_{10}H_8$ ³) have now been used to elucidate the microscopic properties of several cryogenic simple molecular liquids (C_nH_{2n+2} , C_mH_{2m} ; $n = 1, \dots, 4$ and $m = 2, \dots, 4$). Perhaps the most important results of these studies are a glimpse at the intermolecular potential, near

its equilibrium value, for the solvent-solute interaction and an as yet qualitative picture of the solvent-solute cage system. Lifetime studies have revealed that the fluorescence lifetimes of these probes at low temperature are nearly the same as those for the free-molecule limit. However, the solute-solute (excimer) interactions and solute-solvent interactions are quite dependent on the physical properties (size, structure, electron distribution) and energy levels of the solute and solvent molecules.

Toluene, which has energy levels and polarizabilities similar to those of benzene but a dipole moment and a different steric structure, is chosen as a probe for the same set of cryogenic molecular solvents used with benzene,

(1) (a) F. Li, J. Lee, and E. R. Bernstein, *J. Phys. Chem.*, **86**, 3606 (1982); (b) *ibid.*, **87**, 254 (1983).

(2) J. Lee, F. Li, and E. R. Bernstein, *J. Phys. Chem.*, **87**, 260 (1983).

(3) F. Li, J. Lee, and E. R. Bernstein, *J. Phys. Chem.*, previous article in this issue.