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_6 and C_3H_8 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 $\sim$140 ns at $\sim$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 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.

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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

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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}; $n = 1, ..., 4$ and $m = 2, ..., 4$). 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,

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(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.

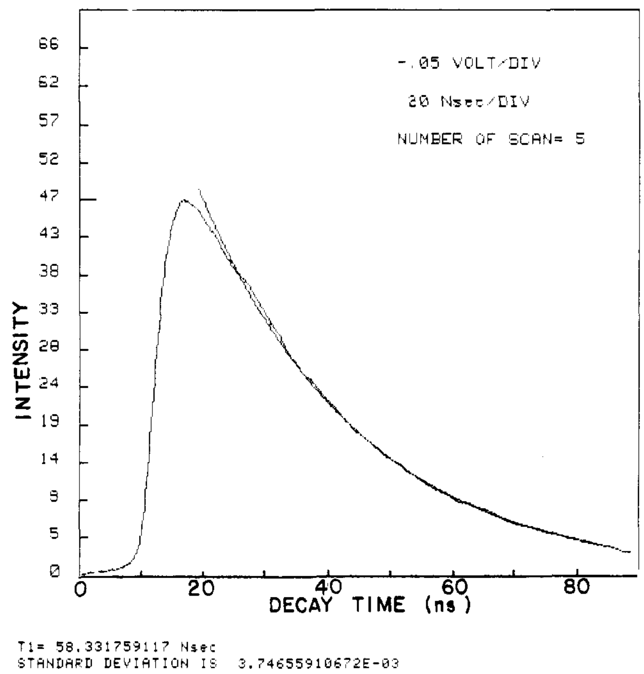

Figure 1. Typical fluorescence decay signal of C_7H_8 in C_2H_6 collected with a Tektronix 7912AD programmable digitizer. The line through the data is a least-squares computer fit to the decay with $\tau = 58.3$ ns and a standard deviation of $\sigma = 3.7 \times 10^{-3}$.

naphthalene, and pyrazine. The comparisons between toluene and the other probe systems thus far employed (especially benzene) should prove an important test of previous ideas concerning potentials and kinetics.

Toluene is a well-studied molecule and its first excited singlet state $^1B_1$ has been investigated via absorption and fluorescence lifetimes in the gas phase[4,5] and by molecular-jet measurements.[6] In this work we study the $^1B_1 \leftrightarrow {}^1A_1$ transition of toluene with particular attention paid to gas-to-liquid shifts, line widths, and their temperature dependences, Franck–Condon shifts, and fluorescence lifetimes as a function of concentration and solvent. Because absolute evaluations require extensive ab initio calculations that are not even possible for benzene,[1] the present toluene study is best understood in comparison to the results for benzene. In corresponding solvent environments, the toluene intermolecular potentials and interactions are nearly identical with those found for benzene. Steric hindrance to excimer formation is responsible for the concentration and temperature independence of the $^1B_1$ lifetime. And finally, the adjacent triplet states of propene and 1-butene solvents are responsible for the additional deactivation channel for both toluene and benzene (but not naphthalene[3]) in these alkene solvents.

Experimental Section

Toluene (Aldrich Gold Label, 99+%) is further distilled through 4-Å molecular sieve, treated with potassium, and well degassed in a high-vacuum manifold. Detailed procedures of solute and solvent purification and instrumental setups are presented in previous reports.[1,2] Fluorescence signals are processed through a Tektronix 7912AD programmable digitizer, with 7A16P and 7B90P plug-ins, which is interfaced to an HP9845S computer. A typical fluorescence decay signal after signal averaging for 320 shots (Figure 1) has an experimental error of less than ±2% (±1 ns for C_7H_8).

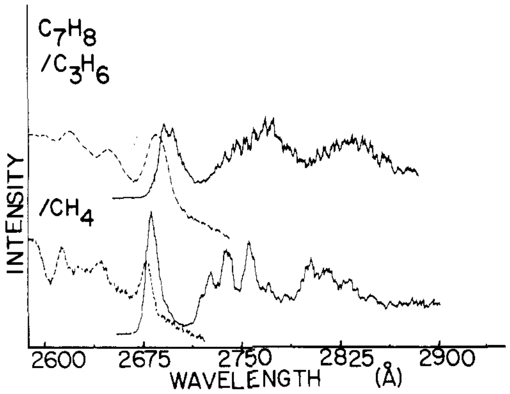

Figure 2. Absorption (- - -) and fluorescence (—) spectra of C_7H_8 in the liquids C_3H_6 and CH_4 at 90 K.

TABLE I: Spectroscopic Data for the $^1B_1 \leftrightarrow {}^1A_1$ Transition of C_7H_8 in Cryogenic Solvents[a]

solvent	0_0^0 [b]	line width	gas-to-liquid shift	Franck-Condon shift
CH_4	37 299	130	−182	35
C_2H_6	37 255	206	−226	78
C_3H_8	37 226	238	−255	98
C_2H_4	37 219	216	−262	108
C_3H_6	37 212	240	−269	104
1-C_4H_8	37 201	238	−280	110

[a] Units: cm^{-1}, error ±20 cm^{-1}. [b] 0_0^0(gas phase): 37 481 cm^{-1} (ref 4).

TABLE II: Spectroscopic Data for the $^1B_{2u} \leftrightarrow {}^1A_{1g}$ in Cryogenic Solvents[a]

solvent	0_0^0 [b]	line width	gas-to-liquid shift	Franck-Condon shift
CH_4	38 112	170	−177	32
C_2H_6	38 042	190	−247	58
C_3H_8	38 019	190	−270	69
C_2H_4	38 036	208	−253	96
C_3H_6	38 010	190	−279	119
1-C_4H_8	37 986	208	−303	124

[a] Units: cm^{-1}, error ±20 cm^{-1}. [b] 0_0^0(gas phase): 38 289 cm^{-1} (ref 1a).

Results

Figure 2 shows the absorption and fluorescence spectra for toluene in CH_4 and C_3H_6 solvents at 90 K. Tables I and II summarize the 0_0^0frequencies, spectral line widths, gas-to-liquid shifts, and Franck–Condon shifts for toluene in CH_4, C_2H_6, C_3H_8, C_2H_4, C_3H_6, and 1-C_4H_8. Within the experimental error of ±20 cm^{-1}, the line widths and frequency shifts are nearly identical with those found for benzene in the same solvents. Even the unsymmetrical broadening to the low-energy side of the fluorescence lines as temperature increases (Figure 3) is reproduced for toluene; the absorption line widths, as found previously for all probe systems, are not altered by changing the temperature.

Fluorescence lifetimes as a function of temperature and solvent are plotted in Figure 4. Varying the concentration from 0.5 to 30 ppm has no effect on the fluorescence lifetime of toluene. However, two different types of solvent effects are evident in Figure 4. In CH_4, C_2H_6, C_3H_8, and C_2H_4 solvents (top curves) the lifetime of toluene is roughly

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[4] N. Ginsburg and W. W. Robertson, *J. Chem. Phys.*, 14, 51 (1946).

[5] (a) M. Jacon, C. Lardenx, R. Lopez-Delgado, and A. Tramer, *Chem. Phys.*, 24, 145 (1977); (b) G. M. Breuer and E. K. C. Lee, *Chem. Phys. Lett.*, 14, 404 (1972).

[6] (a) J. B. Hopkins, D. E. Powers, and R. E. Smalley, *J. Chem. Phys.*, 72, 5039 (1980); (b) J. B. Hopkins, D. E. Powers, S. Mukamel, and R. E. Smalley, *ibid.*, 72, 5049 (1980).

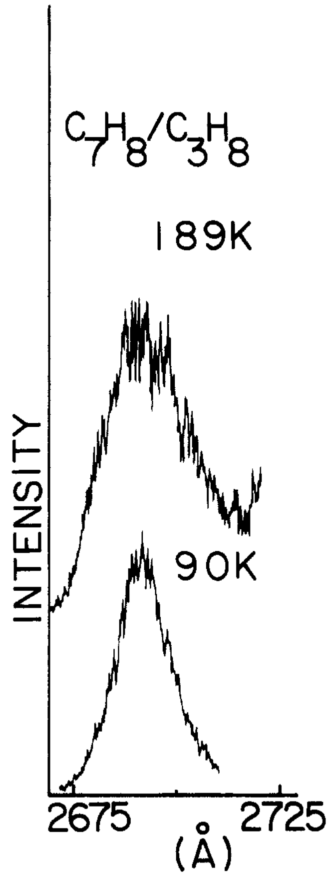

Figure 3. Temperature broadening of the fluorescence line width of the C_7H_8 0_0^0 transition.

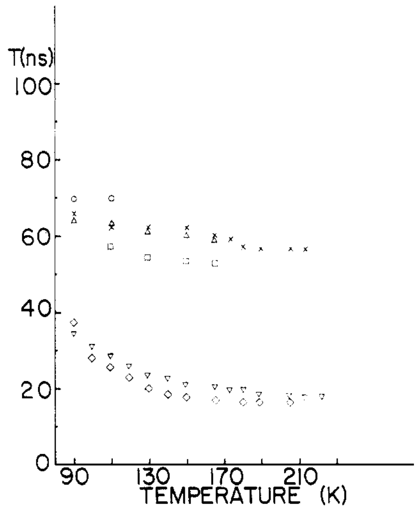

Figure 4. Fluorescence lifetimes of C_7H_8 as functions of temperature and solvent: (O) CH_4, (△) C_2H_6, (X) C_3H_8, (□) C_2H_4, (▽) C_3H_6, (◇) 1-C_4H_8.

insensitive to temperature variation and close to the free-molecule value of 70 ns at low temperature. However, in C_3H_6 and 1-C_4H_8 solvents the lifetime of toluene decreases by more than a factor of 2 as temperature increases, eventually reaching a value of ~17 ns at ca. 200 K.

Discussion

Intermolecular Potentials and Interactions. The analysis of the toluene data presented in the last section can, in principle, be carried out much the same as has been reported for benzene.[1] However, less is known about the states of toluene and some reference point is needed for the analysis of the potentials and interactions between solute and solvent. Thus, most of this section deals with a comparison to benzene for which a more fundamental model system can be assumed.

Spectral line widths and energy shifts for solute molecules as a function of temperature and solvent can provide useful information on the microscopic properties of liquids. Examples of such properties are, for benzene, pyrazine, and naphthalene, cage size of solvents and intermolecular potentials and interactions. Such studies fall into two different categories: a solute molecule in different solvent environments and different solute molecules in the same solvent environment. The previous studies of benzene in various cryogenic solvents[1a] represent an example of the first category. This investigation shows that decreasing Franck–Condon and gas-to-liquid shifts imply a decrease in solute–solvent interaction and an increase in solute–solvent separation (or cage size). The temperature-dependent fluorescence line width, on the other hand, predicts a smaller solvent cage for the excited-state than for the ground-state solute (benzene).

Consideration of benzene and naphthalene in a single solvent, an example of the second catagory of study, leads to the conclusion that the smaller line widths and Franck–Condon shifts for naphthalene with respect to benzene indicated a smaller change in cavity size and intermolecular interaction upon excitation for naphthalene than benzene. This observation scales with polarizability arguments. In spite of this difference, the trends in both solute–solvent systems parallel one another nearly exactly. Neither data set, however, is completely explicable in terms of a simple two-parameter Lennard-Jones potential model for both ground- and excited-state interactions.[3]

Toluene, which has a dipole moment of 0.36 D in the ground state, might be expected to evidence some spectroscopic, and thus interaction, differences in comparison with benzene. One might particularly expect such differences for solvent systems with dipole moments, such as propane, propene, and 1-butene. Nonetheless, the results, presented in Table I, do not show any appreciable difference from those found for benzene for gas-to-liquid shifts, line widths, and Franck–Condon shifts. Hence, it seems quite clear on the basis of all these aromatic hydrocarbon studies that solvent and solute dipole moments are not important parameters for the short-range interactions found in simple molecular liquids. It is concluded that the intermolecular potentials and solvent cage structure are nearly identical in toluene and benzene.

Lifetimes in CH_4, C_2H_6, C_3H_8, and C_2H_4 Solvents. At concentrations as low as 0.5 ppm in these alkane solvents and C_2H_4, the toluene fluorescence lifetime (~70 ns) shows little dependence on temperature. Similar results are reported for benzene. This low-temperature value yields an extrapolated room-temperature lifetime for toluene of ~55 ns, a value considerably higher than the measured ~39-ns lifetime reported for cyclohexane at room temperature.[7] Hence, the "third decay channel",[5a] responsible for the shorter lifetimes observed in room-temperature liquids and high-pressure gases, is not open for toluene in these cryogenic solvents. Again, qualitatively identical results are found for benzene and naphthalene.

Unlike benzene, however, the fluorescence lifetime of toluene does not decrease as the concentration is increased from 0.5 to 30 ppm. In other words, there is no formation of excimers in these solvents over this concentration range. This observation can be rationalized by consideration of steric effects and the binding energy for toluene excimers.

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(7) J. B. Birks, "Photophysics of Arometic Molecules", Wiley-Interscience, New York, 1970.

TABLE III: First Excited-State Energy (cm^{-1}) of C_6H_6, C_6D_6, C_7H_8, and $C_{10}H_8$ in C_3H_6 and 1-C_4H_8 Solvents

	solute			
solvent	C_6H_6	C_6D_6	C_7H_8	$C_{10}H_8$
C_3H_6 (34 522)[a]	37 814	38 010	37 212	31 720
1-C_4H_8 (34 038)[a]		37 986	37 201	31 732

[a] Triplet-state energies of C_3H_6 and 1-C_4H_8 (ref 11).

It has been shown in room-temperature liquids that benzene and its methyl derivatives form excimers of the ring-to-ring or "sandwich" type.[8] Further evidence for a sandwich excimer is provided in recent molecular supersonic jet measurements on benzene clusters,[9] although T-shaped dimers are suggested for the benzene ground state. Presence of the methyl group on the ring perturbs the sandwich excimer and limits the probability of excimer formation due to methyl–methyl interferences. In addition, the excimer binding energy, obtained from concentration- and temperature-dependent fluorescence yield measurements, was found to be reduced by methyl substitution of the benzene ring.[10] The binding energy for the benzene excimer is 0.22 eV and for the toluene excimer is 0.17 eV. Thus, the toluene excimer is less stable and harder to form in the solutions under consideration and consequently plays little role in the overall solution kinetics for the $^1B_1$ excited state in these liquids within the experimental temperature and concentration range.

Lifetimes in C_3H_6 and 1-C_4H_8 Solvents. In C_3H_6 and 1-C_4H_8 solvents, the fluorescence lifetime of toluene decreases from 38 ns at 90 K to 17 ns at about 200 K. The same qualitative behavior, which is independent of concentration, has been observed for benzene[1b] but not naphthalene.[3] These observations strongly suggest that solvent quenching of the first excited singlet states of C_6H_6 and C_7H_8 might play an important role in the fluorescence lifetimes for aromatic hydrocarbons in these alkene solvents. The triplet states of C_3H_6 and 1-C_4H_8 lie just below the first excited singlet states of C_6H_6 and C_7H_8 but above the $^1B_{3u}$ state of naphthalene. These data are given in Table III. It is thus plausible that solvent triplet states can quench the first excited singlet state fluorescence in C_6H_6 and C_7H_8 but not $C_{10}H_8$.

Although both C_6H_6 and C_7H_8 suffer similar overall fluorescence quenching in C_3H_6 and 1-C_4H_8, it is also clear that their detailed behavior must be somewhat different. For example, the lifetime for C_6H_6/C_3H_6, 1-C_4H_8 at 90 K is roughly the gas-phase collisionless values of 100 ns,[1b] while C_7H_8/C_3H_6, 1-C_4H_8 has a lifetime at 90 K (38 ns) about one-half its collisionless gas-phase value (70 ns). These toluene results can be understood in the same context as the benzene results presented previously. The total decay rate for benzene or toluene fluorescence can be treated through an activation energy argument. Then the total rate constant for fluorescence decay becomes

$$k = k_0 + k_Q{}^0 \exp[-\Delta E_a/k_B T] \qquad (1)$$

in which k is the total rate constant for either benzene or toluene, k_0 is the non-temperature-dependent rate constant (including intramolecular radiative and nonradiative rates), the second term in eq 1 gives the temperature-dependent solvent-quenching contribution, and ΔE_a is the activation energy for the temperature-dependent process. k_0 for benzene is (100 ns)$^{-1}$, which is the collisionless gas-phase rate constant, but k_0 for toluene is assumed to be (38 ns)$^{-1}$, which is about one-half the free-molecule value. This added temperature-independent contribution to the toluene rate constant for decay can be thought of as due to energy transfer between solute and solvent due to the better overlap between the two excited solvent and solute states and a larger transition moment for the toluene transition.

Fitting the experimental data for both systems in C_3H_6 and 1-C_4H_8, we obtain activation energies of 233 cm^{-1} for toluene and 445 cm^{-1} for benzene. As pointed out previously, the benzene activation energy suggests a "diffusion" (encounter or solvent orientation) controlled collisional deactivation (energy transfer) process. The toluene–solvent interaction, on the other hand, shows a lower barrier to fluorescence deactivation and thus a more efficient temperature-dependent solvent-quenching process. The two toluene processes k_0 and $k_Q{}^0$ can be thought of as temperature (collision) independent and dependent energy transfer with the energy for the activated process being lower than that of benzene. This lower activation can be due to either a combination of processes with small and high activation energies (i.e., 0 and 450 cm^{-1}) or simply a longer range single process. The toluene energy levels are closer to those of the solvent than are benzene's and the transition moment for the toluene transition is larger than that for benzene. Given the experimental data, it is difficult to separate these two possible situations.

Conclusions

Three main conclusions can be drawn from the above spectroscopic and lifetime studies of toluene in cryogenic liquids.

1. The strength and nature of the intermolecular interactions in hydrocaron liquids are nerly identical for toluene and benzene even though many of the molecular properties of toluene are different from those of benzene. This conclusion is based on spectroscopic data encompassing line widths of absorption and emission, their temperature dependence, Franck–Condon shifts, and gas-to-liquid shifts.

2. Due to steric hindrance and small binding energy for C_7H_8 excimers, no excimer formation could be detected in C_7H_8 cryogenic solution fluorescence lifetimes over the concentration range 0.5–30 ppm.

3. The fluorescence lifetime reduction in toluene C_3H_6 and 1-C_4H_8 solutions is similar to that found for benzene in these liquids. Naphthalene has been found not to evidence such behavior. On the basis of these data and comparisons, the solvent triplet-state quenching mechanism is further supported.

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

Registry No. CH_4, 74-82-8; C_2H_6, 74-84-0; C_3H_8, 74-98-6; C_2H_4, 74-85-1; C_3H_6, 115-07-1; 1-C_4H_8, 106-98-9; toluene, 108-88-3; benzene, 71-43-2.

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