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Absorption spectrum of the 2600 Å transition of benzene in cryogenic liquids^{a)}

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Absorption spectra of the 2600 Å system (${}^1B_{2u} \leftarrow {}^1A_{1g}$) of benzene dissolved in cryogenic liquids N_2 , CO, CF_4 , CH_4 , NF_3 , C_2H_6 , and C_3H_8 are obtained and reported. As in the gas phase spectrum, the dominant series is the vibronically induced $6_0^1 1_0^n$ ($n = 1, \dots, 5$). No rotational or hot band structure has been observed in any of the solvents. The following features have been identified in the spectra: $6_0^1 1_0^n$, $6_0^2 1_0^n$, $6_0^1 8_0^1 1_0^n$, $6_0^1 9_0^1 1_0^n$, $6_0^1 8_0^1 9_0^1 1_0^n$, and $6_0^1 7_0^1 1_0^n$. In addition, N_2 , CO, CF_4 , NF_3 , and CH_4 induce the (0,0) and 1_0^1 transitions while C_2H_6 and C_3H_8 induce $6_0^1 1_0^n$ and 6_0^2 . Linewidths range from 50 cm^{-1} (N_2) to 250 cm^{-1} (C_3H_8) and are temperature independent for a given solvent. Gas to liquid shifts are found to vary from -250 to -300 cm^{-1} throughout the series of solvents used and to be temperature independent. Solvent perturbations are in general unique and characteristic of particular solvents.

I. INTRODUCTION

Simple molecular systems such as N_2 , O_2 , and CO have been employed to study vibrational energy relaxation and transfer processes in the liquid state.¹ These results have stimulated theoretical efforts in the area, summarized recently by Oxtoby.² On the other hand, cryogenic liquids have been employed to study molecular systems in a low temperature environment.³

Spectra of molecules dissolved in cryogenic liquids evidence no rotational structure and no hot bands; spectra of such solutions are thereby typically simpler and less congested than gas phase spectra. In particular, rotational half-widths estimated for C_6H_6 are much too small to account for the linewidths reported in this work. Low temperature crystal and matrix isolation absorption spectra, while removing the above difficulties, often generate extra features peculiar to the specific system investigated. It is thus possible to obtain information about a given molecular system in a cryogenic liquid not readily obtained from either gas or crystal phase spectroscopy. Since solution spectra are often simplified for cryogenic solvents, it is, moreover, possible to reverse the study and take advantage of a well investigated and well understood molecule to probe the microstructure of simple cryogenic liquids.

In this paper we report the spectra of the 2600 Å transition of benzene (${}^1B_{2u} \leftarrow {}^1A_{1g}$) observed in different cryogenic liquids: N_2 , CO, CF_4 , NF_3 , CH_4 , C_2H_6 , and C_3H_8 . The immediate goal of this work has been to demonstrate the feasibility of obtaining detailed spectra of medium size molecules like benzene in cryogenic liquids; indeed, solubilities of C_6H_6 , $C_4N_2H_4$, C_5NH_5 , OsO_4 , and others are sufficient to allow such studies. The major long range goal of this particular work is to determine the feasibility of using molecular probe systems to learn about simple liquids through spectroscopic studies. Not only has it been possible to observe frequency and intensity differences as a function of cryogenic solvent, but new features have been

observed in the benzene spectrum as well. A previous investigation of benzene in liquids around 150–200 K was of too low resolution to show any detail.⁴

The 2600 Å system of benzene has been assigned as ${}^1B_{2u} \leftarrow {}^1A_{1g}$, vibronically induced, based on detailed analyses of spectra^{5,6} and various theoretical arguments.⁷ The transition is induced by vibrations of e_{2g} (D_{8h}) symmetry which couple the dipole allowed E_{1u} and B_{2u} states. The most effective e_{2g} vibronic mixing is caused by the ν_8 mode (C–C–C bending), which has a frequency of 606 cm^{-1} in the A_{1g} ground state and 521 cm^{-1} in the B_{2u} excited state. Hence, the intense vibronic series $6_0^1 1_0^n$ ($n = 0, 1, \dots$) dominates the 2600 Å system.

In the liquid state, it is expected that a molecule will experience reduced symmetry, and therefore other transitions, such as the (0, 0) or 1_0^1 etc., may be induced. The intensity, position, and shape of these induced transitions may in turn be investigated, theoretically and experimentally, to obtain information on the molecule's environment. This is not dissimilar from the situation found in low temperature solids. Experimental results reported in this paper show general agreement with these expectations. A number of new transitions are assigned for C_6H_6 involving ν_7 , ν_8 , and ν_9 , and several interesting intensity perturbations are characterized as a function of solvent.

II. EXPERIMENTAL

Studies reported in this work are of a conventional UV absorption nature: xenon lamp light source, 1 m monochromator with a 2400 grooves/mm grating, and photon counting detection with RCA C31000M or EMI9789QB photomultiplier tubes and PAR and Ortec electronics. Monochromator slits were typically 10–20 μm . The sample cell is a cube of 15 ml total volume with three 1 in. diameter Supracil quartz windows. The light path is roughly 3.8 cm. This cell is attached to a Cryodine mechanical helium refrigerator (CTI-350) which has an ultimate low temperature of 12 K. The cell is in a vacuum chamber and surrounded by a heat shield. Temperature is controlled ($\pm 0.1\text{ K}$) by a heater

^{a)}Supported in part by a grant from the National Science Foundation.

placed at the base of the cold station of the refrigerator. Two temperature sensors, one for temperature control and the other for readout, are located at the bottom of the cold head and cell, respectively. Heater and sensors are connected to a Lake Shore DTC-500SP temperature controller, which automatically monitors heater current and maintains constant temperature at the cell.

Benzene (Fischer Gold Label) is further purified by vacuum distillation over potassium to remove water and other oxygen-containing impurities. Solvents are all research grade of highest attainable commercial purity. Solvents such as CF_4 , C_2H_6 , NF_3 , C_3H_8 , and CO are further purified by passing through a molecular sieve of the appropriate size and by outgassing at 77 K. To remove N_2F_4 and N_2F_2 from NF_3 , the material is passed through nickel powder at 230 °C and then a molecular sieve again. Gas samples for deposit in the liquid cell are prepared by mixing solute and solvent at room temperature in a 7 l container. The concentration of the mixture is carefully controlled by temperature variation of solute vapor pressure in a well calibrated volume. All of these vacuum operations are carried out in vacuum systems with working pressures of 2×10^{-7} Torr.

The gas phase mixture is transferred and condensed into the sample cell at high rates to prevent separation in the fill tube. In order to increase transfer speed and efficiency, the cell is precooled to 10 K below the solvent's melting point and a heater is applied to the transfer tube to prevent condensation of the solute outside the cell. The temperature of the sample cell is always maintained within the liquid range after condensation.

UV spectra were taken only for solutions that were clear and totally transparent. As with solutions near room temperature, it is possible to vary temperature of the solution over its liquid range and to observe the solute precipitate and dissolve with the changes.

It is somewhat surprising that these cryogenic liquids are good solvents, but a simple calculation based on ideal solution theory can show that reasonable solubilities can be predicted if Raoult's law is obeyed for the mixture. It is straightforward to derive the ideal solution behavior for the solubility (mole fraction of solute) in an ideal solvent as⁸

$$\ln s = \left(\frac{L_m - \Delta C T_m}{R} \right) \left(\frac{1}{T_m} - \frac{1}{T} \right) + \frac{\Delta C}{R} \ln \left(\frac{T}{T_m} \right).$$

TABLE I. Maximum concentration and temperature of benzene solutions (solubilities determined visually by disappearance of precipitate as a function of temperature).

Solvent	Concentration (ppm)	Temperature (K)	Figure
N_2	8 ± 3	77	1
CO	8 ± 3	77	2 (top)
CF_4	8 ± 3	100	2 (bottom)
C_2H_6	35 ± 5	100	3 (bottom)
C_2H_6	150 ± 5	150	3 (top)
NF_3	8 ± 3	90	

TABLE II. Assignments of $\text{C}_6\text{H}_6/\text{C}_2\text{H}_6$, 150 ± 5 ppm, 150 K.

Vacuum wavelength (Å)	Vacuum wave number (cm^{-1})	Difference (cm^{-1})	Assignment
2643.3	37 826	0	00
2607.8	38 347	521	6_0^1
2575.8	38 823	997	6_0^2
2546.2	39 273	1447	$6_0^1 1_0^1$
2531.8	39 497	1671	$6_0^1 9_0^1$
2513.8	39 781	1955	$6_0^1 8_0^1$
2487.7	40 197	2371	$6_0^1 1_0^2$
2473.8	40 423	2597	$6_0^1 1_0^1 9_0^1$
2456.6	40 707	2881	$6_0^1 1_0^1 8_0^1$
2443.1	40 931	3105	$6_0^1 8_0^1 9_0^1$
2432.0	41 119	3293	$6_0^1 1_0^3$
2418.6	41 347	3521	$6_0^1 1_0^2 9_0^1$
2415.6	41 397	3571	$6_0^1 7_0^1$
2402.1	41 631	3805	$6_0^1 1_0^2 8_0^1$
2389.1	41 857	4031	$6_0^1 1_0^1 8_0^1 9_0^1$
2378.9	42 037	4211	$6_0^1 1_0^4$
2365.8	42 269	4443	$6_0^1 1_0^3 9_0^1$
2362.8	42 323	4497	$6_0^1 1_0^1 7_0^1$
2350.0	42 553	4727	$6_0^1 1_0^3 8_0^1$
2337.5	42 781	4955	$6_0^1 1_0^2 8_0^1 9_0^1$
2328.2	42 951	5125	$6_0^1 1_0^5$
2315.5	43 187	5361	$6_0^1 1_0^4 9_0^1$
2312.3	43 247	5421	$6_0^1 1_0^2 7_0^1$

In this equation the following definitions are used: s = solubility at saturation = $N_2/(N_1 + N_2)$; L_m = solute latent heat of fusion at the melting point; $\Delta C = (C_{\text{liq}} - C_{\text{cryst}})$ = [(heat capacity at constant pressure of liquid solute) - (heat capacity at constant pressure of crystal solute)]; T_m = melting point temperature of solute; and R = gas constant = 2 cal/K mol. Since this equation pertains to an ideal Raoult's law solution, the solubility is independent of the nature of the solvent. Clearly, the equation is highly approximate, but for close to ideal behavior in dilute solutions it should be possible to predict whether or not spectroscopy will be possible in, for example, a 1–10 cm path length of liquid solvent. Indeed, for benzene in liquid nitrogen at 77 K we calculate a solubility of ~ 200 ppm using $L_m \sim 2.3$ kcal, $\Delta C \sim 3.7$ cal/K mol, and $T_m \sim 280$ K.

III. RESULTS AND DISCUSSION

Table I summarizes maximum concentrations, operating temperatures, and corresponding figures for five different solvents. Table II summarizes the full absorption spectrum of the 2600 Å system in ethane.

In general, all spectra show an average gas to liquid shift of $-275 \pm 25 \text{ cm}^{-1}$; these data are given in detail

TABLE III. Gas to liquid shift,^a linewidth, intensity ratio, and enhancements of ${}^1B_{2u} \leftarrow {}^1A_{1g}$ transition features for various solvents.

Solvent	Origin (cm ⁻¹)	L-G shift (cm ⁻¹)	Linewidth (cm ⁻¹)		Intensity ratio		Intensity enhancement ^b
			6_0^1	$6_0^1 1_0^1$	(0, 0)/ 6_0^1	$1_0^1/6_0^1$	6_0^1
N ₂	37 808	-278	59(77 K)	77	0.44	0.34	1
CO	37 802	-284	110(77 K)	123	0.44	0.43	1
CF ₄	37 786	-300	132(100 K)	154	0.57	0.34	1
C ₂ H ₆	37 826	-260	162(100 K)	152	0	0	2
C ₃ H ₈	37 814	-245	220(90 K)	177	0	0	2

^aThe origin in the gas phase spectrum is 38 086 cm⁻¹ (Ref. 6).

^bEstimated by setting the 6_0^1 absorption intensity in N₂ to be 1 and then comparing to other solvents at a fixed concentration (5 ppm). It is assumed that intensity is linearly proportional to concentration.

in Table III along with intensity determinations. No hot band or rotational structure for any benzene transition is observed. The major gas phase progression $6_0^1 1_0^n$ ($n = 1, \dots, 5$) dominates the spectrum as expected; the average value for ν_1 in the ${}^1B_{2u}$ state for all solvents, as obtained for this series, is 922 cm⁻¹. However, as can be seen in Table III, the intensity of the $6_0^1 1_0^n$ series is about a factor of 2 larger in C₂H₆ and C₃H₈ solvents than in CH₄, CF₄, NF₃, or diatomic solvents.

Although the origin transition is not allowed in the D_{6h} point group, it can be induced in the liquid state through environmental perturbations. The intensity ratio of this induced feature can be found in Table III. The ratio of (0, 0)/ 6_0^1 intensity drops by more than a factor of 10 for C₂H₆ and C₃H₈ compared to the other solvents. Clearly, there are substantial environmental and interaction differences between the two sets of solvents.

The band at 920 ± 2 cm⁻¹ from the origin in N₂, CO, and CF₄ solvents (Figs. 1 and 2) is assigned to be a direct observation of 1_0^1 . Thus, 1_0^1 becomes an allowed member of the Franck-Condon progression built on the allowed origin. It would appear that both features (0, 0) and 1_0^1 are of similar intensity. In C₂H₆ or C₃H₈ (Fig. 3),

however, no such feature is apparent, most likely because the (0, 0) is so weak for these two solvents.

At higher concentrations (~150 ppm) in C₂H₆ (Fig. 3) and C₃H₈ solutions, a band is observed at 997 cm⁻¹ from the origin between 6_0^1 and $6_0^1 1_0^1$. Since the 6_0^1 transition in both of these solvents is greatly enhanced in intensity, the feature is assigned as 6_0^2 (see Table II). Although it has not been directly observed in the gas phase,⁶ a value of 1036 cm⁻¹ has been suggested for 6_0^2 . This value is about 40 cm⁻¹ higher than that assigned here; the most likely explanation for this difference is a solvent perturbation.

In addition to ν_8 , modes ν_7 , ν_8 , and ν_9 also have e_{2g} symmetry and may therefore be observed as false vibronic origins in the 2600 Å system. They have, however, been determined to be much less effective

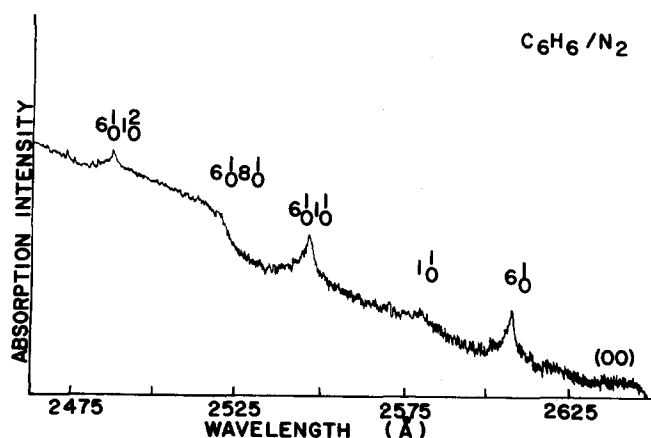


FIG. 1. The absorption spectrum of the ${}^1B_{2u} \leftarrow {}^1A_{1g}$ transition of C₆H₆ in liquid N₂ at ~8 ppm and 75 K.

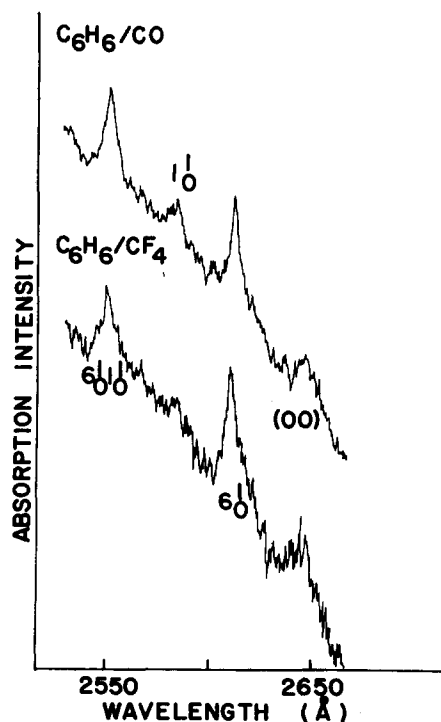


FIG. 2. The absorption spectrum of the ${}^1B_{2u} \leftarrow {}^1A_{1g}$ transition of C₆H₆ in liquid CO (top) and CF₄ (bottom) at 8 ppm.

in mixing B_{2u} and E_{1u} electronic states and may be expected to appear only in combination with ν_8 or one of its series. In the gas phase spectrum ν_7 has been identified with the Q_0^0 series⁵ but ν_8 and ν_9 have not been positively identified. In cryogenic liquids, transitions have been observed that are quite close to expected values for all three e_{2g} modes.

The feature at 3077.2 cm^{-1} in the gas phase has been assigned^{5,6} as 7_0^1 and it also has been identified in matrix isolation spectra.⁹ In this work, 7_0^1 is observed as a shoulder on $6_0^1 8_0^1 1_0^1$ and in the series $7_0^1 6_0^1 1_0^1$ of C_2H_6 and C_3H_8 solutions. The frequency for ν_7 is 3050 cm^{-1} (Tables II and IV).

ν_8 is expected to appear only in combination with ν_8 based on estimates for the gas phase spectrum.⁶ In C_2H_6 and C_3H_8 solutions, $6_0^1 1_0^1$ obscures the region ($\sim 1450 \text{ cm}^{-1}$) in which 8_0^1 might be expected so no direct determination of it is possible. However, we do observe the new series $8_0^1 6_0^1 1_0^1$ (Table III). The calculated value of ν_8 is 1434 cm^{-1} (Table IV).

Like ν_7 and ν_8 , ν_9 shows the combination progression $9_0^1 6_0^1 1_0^1$. The value obtained for ν_9 is 1150 cm^{-1} . Although a tentative assignment for ν_9 has been suggested⁶ at 950 cm^{-1} , we feel the value of 1150 cm^{-1} fits in well with the expected progression and a value of 1148 cm^{-1} derived from single vibronic level fluorescence data.¹⁰ Moreover, the series $8_0^1 9_0^1 6_0^1 1_0^1$ has been identified and the value for $8_0^1 9_0^1$ is in good agreement with that of the individual normal modes (Table IV).

In addition to intensity enhancements ($6_0^1 1_0^1$ in C_2H_6), induced features [(0, 0) and 1_0^1 in N_2], and gas to liquid shifts, we are also able to obtain linewidth data for the $6_0^1 1_0^1$ progression in each solvent. These data are summarized in Table III. Quite interestingly, linewidths are temperature independent for a given solvent (often over a range of 75 K), but vary considerably from sol-

TABLE IV. Summary of vibrational frequencies of ν_1 , ν_8 , $2\nu_6$, ν_7 , ν_8 , ν_9 , and $\nu_8 + \nu_9$ in the $^1B_{2u}$ state.

Vibrational mode	Vibrational frequencies (cm^{-1})
ν_1	922
ν_8	521
$2\nu_6$	997
ν_7	3050
ν_8	1434
ν_9	1150
$\nu_8 + \nu_9$	2584

vent to solvent. For example, the linewidth changes by almost a factor of 5 upon going from N_2 and NF_3 to C_3H_8 .

IV. CONCLUSIONS

Cryogenic solvents employed in this study of the 2600 Å system of benzene seem to fall into two categories distinguished by their perturbing effects on the spectrum. The small molecular systems (N_2 , CO , CF_4 , NF_3 , and CH_4) induce the origin series [(0, 0) and 1_0^1] and do not enhance the $6_0^1 1_0^1$ series much above that observed in the gas phase. Linewidths for $6_0^1 1_0^1$ transitions range between 50 and 150 cm^{-1} for these solvents. On the other hand, the larger hydrocarbons C_2H_6 and C_3H_8 do not enhance the origin series but bring out $6_0^1 1_0^1$ and 6_0^2 to such an extent that ν_7 , ν_8 , and ν_9 are all identified in combination with $6_0^1 1_0^1$. In general, all solvents produce a spectrum red shift which varies from solvent to solvent at $\sim -275 \pm 25 \text{ cm}^{-1}$. This shift is smallest for C_2H_6 and C_3H_8 and largest for CF_4 . Linewidths, red shifts, and intensities are all temperature independent over the normal liquid ranges of the respective solvents.

Due to the relatively sharp line spectra obtained in many solvents, the lack of rotational structure, and the absence of hot band congestion, cryogenic liquids evidence a great deal of potential for spectroscopic investigations of medium sized molecules. Moreover, a number of interesting and apparently systematic phenomena, such as selective intensity enhancements, linewidth variations, gas to liquid shifts, and temperature independence of most observations, have been identified. It is a major goal of this work to use such data to understand the detailed microscopic structure and dynamics of simple molecular (cryogenic) liquids. We are presently pursuing this avenue both experimentally (i.e., emission, relaxation, and lifetime studies) and theoretically.

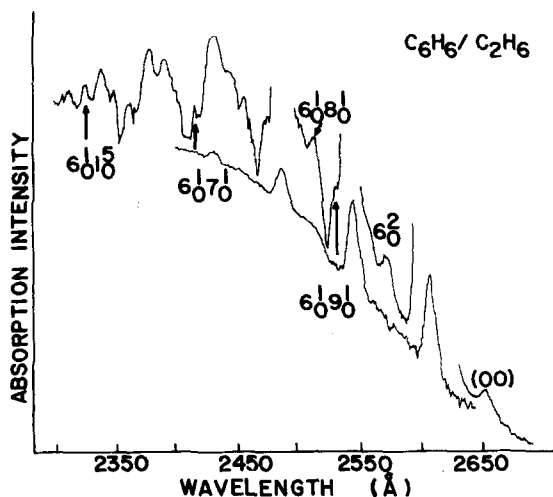


FIG. 3. The absorption spectrum of the $^1B_{2u} \leftarrow ^1A_{1g}$ transition of C_6H_6 in C_2H_4 at ~ 35 ppm and 100 K (bottom) and ~ 150 ppm and 150 K (top).

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