Spectroscopic studies of cryogenic fluids: Benzene in argon and helium

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Citation: The Journal of Chemical Physics **87**, 2457 (1987); doi: 10.1063/1.453086
View online: http://dx.doi.org/10.1063/1.453086
View Table of Contents: http://aip.scitation.org/toc/jcp/87/5
Published by the American Institute of Physics

Spectroscopic studies of cryogenic fluids: Benzene in argon and helium[a)]

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(Received 16 March 1987; accepted 18 May 1987)

Energy shifts and bandwidths of the 6_0^1 vibronic feature of the ${}^1B_{2u} \leftarrow {}^1A_{1g}$ optical absorption spectrum of benzene dissolved in supercritical argon and helium, and in liquid argon are reported as a function of pressure, temperature, and density. Benzene/Ar solutions display red shifts of the 6_0^1 transition with increasing density but the dependence is found to be nonlinear at high densities. Benzene/He solutions evidence blue shifts of the 6_0^1 transition as a function of increasing density which also becomes nonlinear at high densities. Only small spectral shifts are recorded if the density is kept constant and pressure and temperature are varied simultaneously. In addition, a small density independent temperature effect on the transition energy shift is identified. Experimental results are compared to dielectric (Onsager–Böttcher and Wertheim) and quantum statistical mechanical (Schweizer–Chandler) theories of solvent effects on solute absorption energy. Reasonably good agreement between experiment and theory is found only for the benzene/Ar system at relatively low densities. The theory fails to predict energy shifts for both the benzene/He and high density benzene/Ar systems. This result is different from the findings for the benzene/N_2 and benzene/C_3H_8 solutions and can be interpreted qualitatively in terms of competition between dispersive attractive and repulsive interactions as a function of density. The failure of the theory to describe these transition energy shifts is attributed to the omission of explicit repulsive interactions terms in the theoretical models employed.

I. INTRODUCTION

Optical spectroscopic studies of aromatic solute molecules in simple cryogenic solvents have been successfully used to investigate microscopic properties of different solute/solvent systems.[1–6] Structure, interaction potentials, solubility, and dynamics of liquid solutions have been studied at atmospheric pressures. In addition, we have recently shown[7,8] that the optical absorption and emission spectra of aromatic solute molecules dissolved in both cryogenic liquids and fluids can be studied as a function of solution temperature, pressure, and density. Variation of these three experimental parameters generates selective changes in either the intermolecular interaction potential, thermal population of states, or both, which are reflected in the solute optical spectra as transition energy shifts and linewidth changes.

Solution density, being both temperature and pressure dependent, is an important microscopic parameter in the quantum statistical mechanical theory proposed by Schweizer and Chandler (SC)[9] for the interpretation of solute absorption energy shifts in dilute solutions. Therefore, variable density (temperature and pressure dependent) studies are important for the experimental verification of the microscopic theory.

In previous work,[7,8] we have explored in detail the spectroscopic behavior of the benzene ${}^1B_{2u} \leftrightarrow {}^1A_{1g}$ transition in liquid propane and supercritical fluid nitrogen. Absorption and emission red shifts of this electronic transition are linear functions of density for both the benzene/C_3H_8 and benzene/N_2 systems. These experimental shifts can be compared to predictions of both dielectric and microscopic theories of transition energy shifts and interpreted qualitatively in terms of changes occurring in the intermolecular potentials of the ground and excited states.[7] The quantum statistical mechanical SC theory[9] is found to reproduce the normalized relative transition energy shift as a function of density for both benzene/C_3H_8 and benzene/N_2 systems. Dielectric theories, Onsager–Böttcher (OB)[10,11] and Wertheim (W),[10,12] do not relate the transition energy shifts directly to density. Nonetheless, a relatively accurate prediction of transition energy shifts can be obtained for the benzene/N_2 system in the supercritical fluid phase based on the density dependence of the macroscopic optical dielectric constant. Satisfactory theoretical description of the spectroscopic behavior in the two solute/solvent systems studied so far indicates the importance of the long range dispersive dipolar interactions on which the employed theories are based.

In the present paper we describe and interpret the spectroscopic behavior of the ${}^1B_{2u} \leftarrow {}^1A_{1g}$ absorption system of the benzene in argon and helium. These solutions are of interest because argon is reported not to show a linear dependence of the solute energy shift with changing density at high pressures,[13] and helium is reported to generate a density dependent blue shift for solute electronic transitions.[13,14] We find for the benzene/Ar system that the transition energy (red) shift is roughly a linear function of density only at relatively low densities. At high densities, reduction of the energy shift is observed: this is contrary to the predictions of the dielectric and microscopic theories and to the experi-

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[a)] Supported in part by a grant from NSF.

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0021-9606/87/172457-09$02.10

mental results for the benzene/N_2 and benzene/C_3H_8 systems. Thus, in terms of electronic transition energy shifts, argon solutions of benzene are different from nitrogen solutions. This decrease or saturation of the red shift at high density suggests that, in the benzene/Ar system, repulsive exchange interactions, which are not explicitly accounted for by any of the theories, compete effectively with the attractive dispersive interactions thereby reducing the expected red energy shift at high solution densities.[14,15]

In the benzene/He supercritical fluid, repulsions dominate attractions and both band shifts and broadenings behave differently from those found for the benzene/Ar and benzene/N_2 systems.

II. EXPERIMENTAL

The experimental setup is analogous to the one described in detail previously.[7] A conventional UV Xenon lamp (Hanovia), a 1m monochromator (McPherson), and a photon counting system (PAR/Ortec) are used for the measurement of absorption spectra. The sample is contained in high pressure cylindrical cell with a 1 cm^3 volume and a 1.2 cm absorption pathlength. Four cone-shaped sapphire windows are sealed to their holders with Crest 7450 epoxy. A good seal between the window holders and the cell body is achieved using tapered indium coated brass gaskets on the high pressure side, and an indium seal at the low pressure side. Such a double sealing entirely eliminates helium leaks between 100 K and room temperature at pressures up to 3 kbar. Pressure is measured by two resistance pressure transducers (Sensotec) with an absolute accuracy of better than 15 bar. Hand operated generators and valves (High Pressure Equipment Corp.) are used for pressurization. Cell temperature is controlled with a mechanical helium refrigerator to an accuracy ± 2 K.

Known amounts of commercial high purity benzene and argon (helium) are premixed at room temperature in a large calibrated volume and subsequently transferred into the evacuated high pressure system. Benzene concentration (typically 50–400 ppm) varies with temperature and pressure due to variation in solubility, especially at low temperatures and high pressures. Additionally, the number of benzene molecules in the optical path changes with solution density. The absorption band energy is measured with an absolute error of ~ 20 cm^{-1}; the exact error for a particular feature depends, of course, on the bandwidth (temperature and pressure).

III. EXPERIMENTAL RESULTS

A. Transition energy shifts

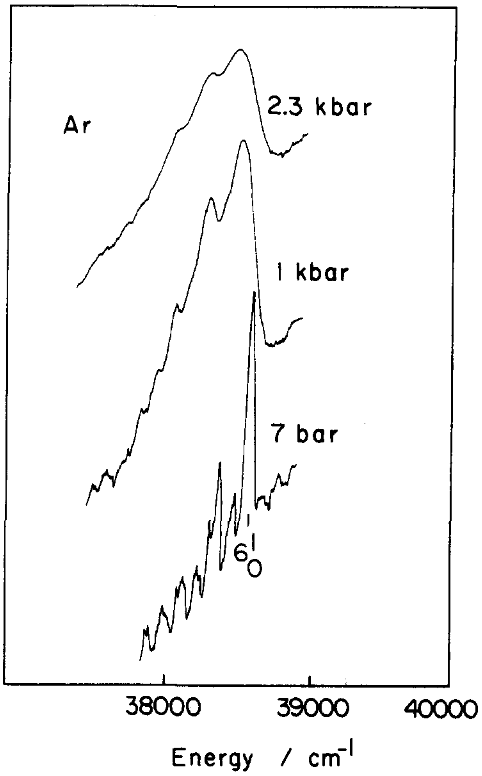

FIG. 1. Typical pressure development of the 6^1_0 absorption band of benzene in argon at room temperature. Note that transition energy shifts to the red and the bands broaden toward the lower energy side of the spectrum as a function of pressure.

Since all the bands in the ${}^1B_{2u} \leftarrow {}^1A_{1g}$ absorption spectrum of benzene behave in a similar manner with respect to changes of transition energy with temperature and pressure, only the results for the most intense 6^1_0 feature of the $6^1_0 1^n_0$ vibronic progression are presented herein. Typical pressure development of the first optical absorption band at room temperature is shown in Figs. 1 and 2 for benzene/Ar and benzene/He, respectively. The energy shifts of the 6^1_0 band are determined at constant temperature and variable pressure, constant pressure and variable temperature, and constant density (simultaneously variable temperature and pressure). The pressure dependences of the transition energy shifts at constant temperature are summarized in Fig. 3. The transition energy is shifted to the red for benzene/Ar

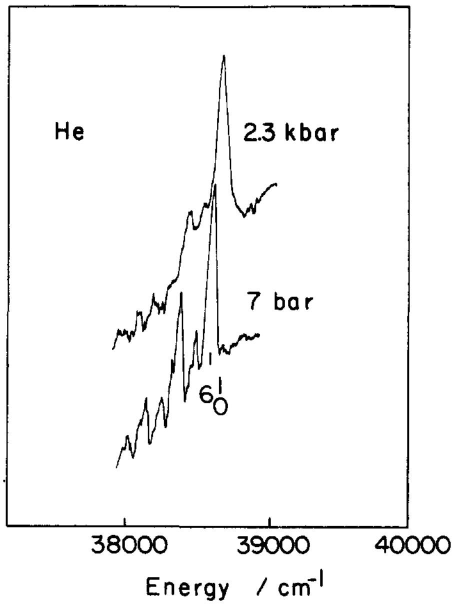

FIG. 2. Pressure development of the 6^1_0 absorption band of benzene in helium at room temperature. Note that transition energy shifts to the blue and the features do not broaden as a function of increasing pressure.

but to the blue for benzene/He. The temperature dependences of the energy shifts at constant pressure are shown in Fig. 4. While red energy shifts are observed with decreasing temperature for benzene/Ar, small blue energy shifts are monitored for benzene/He solutions. We are not able to measure the spectra for benzene/He solutions below ~200 K due the reduced solubility of benzene in helium at these temperatures.

Both the constant temperature variable pressure, and constant pressure variable temperature dependences shown in Figs. 3 and 4 can be expressed as a function of the experimental density calculated from thermodynamic data[16,17] by plotting the energy shifts obtained in those different experiments on the same graph. As shown in Fig. 5, the energy shift for the benzene/Ar solution is a linear function of density only at relatively low densities. The slope of this (linear) dependence is ~6.8 cm^{-1}/100 kg m^{-3}. At densities higher than ~700 kg m^{-3} (0.01 molecules $Å^{-3}$) the energy shift is reduced with further increase of density and almost no density dependence of the transition energy is observed at the highest density (~1500 kg m^{-3} or 0.0226 molecules $Å^{-3}$). The dependence of energy shift on density is the most important and obvious spectroscopic difference between the benzene/Ar, benzene/N_2 and benzene/propane systems.

As reported for the benzene/N_2 system, a small "hysteresis" of the transition energy shift is observed at high densities; the lower the temperature, the smaller is the energy shift for the same constant density (see Fig. 5). This effect, although small, is reproducible and indicates that the energy shift is not only a function of density but depends on temperature as well. Quantitative estimation of the pure temperature effect is difficult because its magnitude is of the order of experimental error. The effect of temperature alone on the solute transition energy can be observed, however, by monitoring transition energy at constant density during simultaneous variations of temperature and pressure. The absorption energy shift at constant density ($\rho = 1200$ kg m^{-3}) is displayed in Fig. 6. The shift is small (but measureable) even though temperature and pressure are widely varied. Nonetheless, absence of a pronounced energy shift at constant density demonstrates the importance of solution density for solute spectroscopic properties. Density is similarly found to be an essential parameter for benzene/N_2 and benzene/propane solutions.

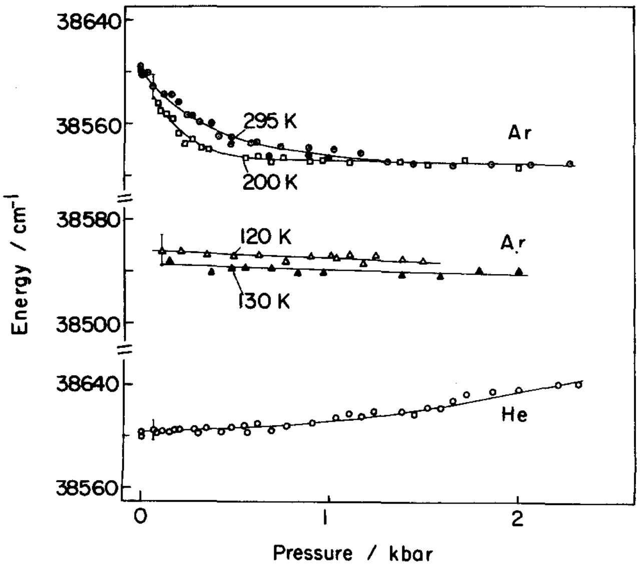

FIG. 3. Pressure dependences of the energy of the 6_0^1 absorption band of benzene in argon (Ar) and helium (He). Dependences for energy shifts in argon are measured in the fluid phase at 200 K (□) and 295 K (⊙) as well as in the liquid phase at 120 K (△) and 130 K (▲). Energy shifts in helium are given at room temperature only.

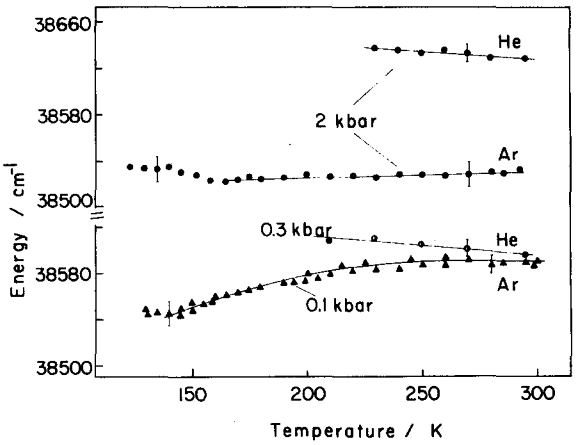

FIG. 4. Temperature dependences of the energy of the 6_0^1 absorption band of benzene in argon (Ar) at 0.1 kbar (▲) and 2 kbar (●), and helium (He) at 0.3 kbar (◑) and 2 kbar (●). The critical temperature of argon is $T_c = 150.86$ K.

The transition energy shift for benzene in helium occurs to the blue with increasing density (see Fig. 5) and is a pronounced nonlinear function of density at high densities. The energy shifts due to an isothermal change of pressure (Fig. 3) and an isobaric change of temperature (Fig. 4) are both comparable functions of the density (Fig. 5). Therefore density is also an important parameter for transition energy shifts in benzene/He system. The blue energy shift for the

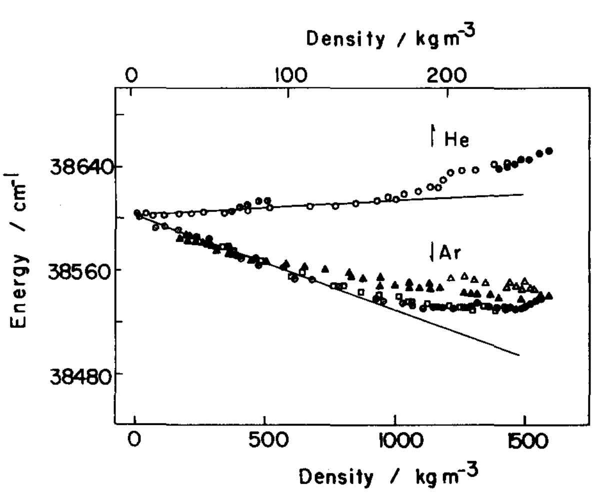

FIG. 5. Transition energies of the 6_0^1 absorption band of benzene taken from Figs. 3 and 4 plotted as a function of experimental density (calculated from the thermodynamic data). For comparison different points are marked in the same way as in Figs. 3 and 4.

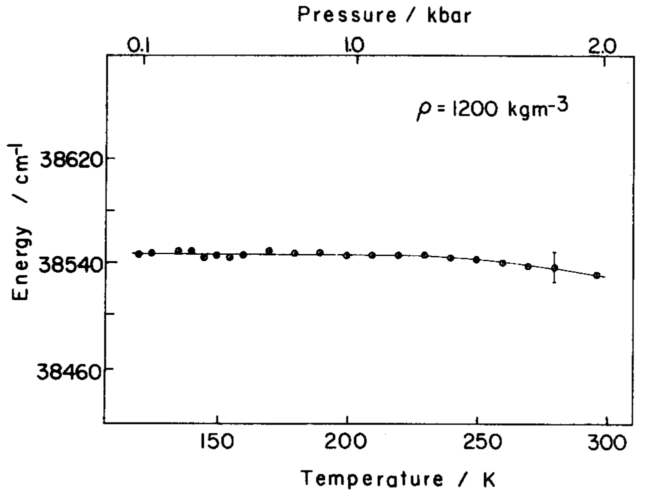

FIG. 6. Transition energy shift of the 6_0^1 absorption band of benzene in argon measured at constant density $\rho = 1200\ \mathrm{kg\ m^{-3}}$ as a function of simultaneously varied temperature and pressure.

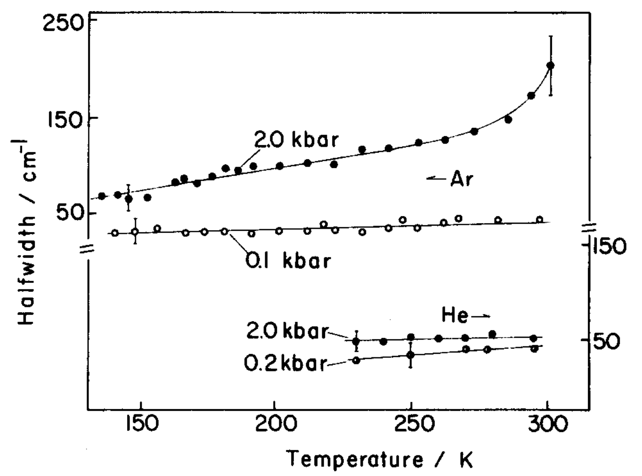

FIG. 8. Temperature dependences of the absorption 6_0^1 band half-widths for benzene in argon (Ar) and helium (He) at two different pressures. The bandwidth of the benzene 6_0^1 band in argon at 2 kbar is obtained by a deconvolution of the overall spectrum. This procedure causes large errors, especially at relatively high temperatures.

benzene/He solution is presumably due to the lack of attractive dispersive interactions and predominance of density dependent repulsive interactions in the system.

B. Linewidths

Comparing Figs. 1 and 2 one can see considerable band broadening toward the low energy side of the spectrum with increasing pressure for the benzene/Ar solution, whereas no comparable pronounced broadening is observed for the benzene/He system. Pressure and temperature dependences of the half-widths at half-maximum of the 6_0^1 bands for benzene/Ar and benzene/He solutions are shown in Figs. 7 and 8. The benzene absorption half-width in argon solution increases considerably with both increasing temperature and pressure in a manner similar to the behavior of benzene/N_2 system.[8] Contrary to the behavior of benzene in nitrogen and argon solutions, absorption bands of benzene in helium do not exhibit pronounced broadening; only small changes in band shapes and bandwidths are observed within large ranges of temperature and pressure (seen in Figs. 7 and 8). Thus, in terms of band broadening, the benzene/He system is different than benzene/Ar and benzene/N_2 solutions.

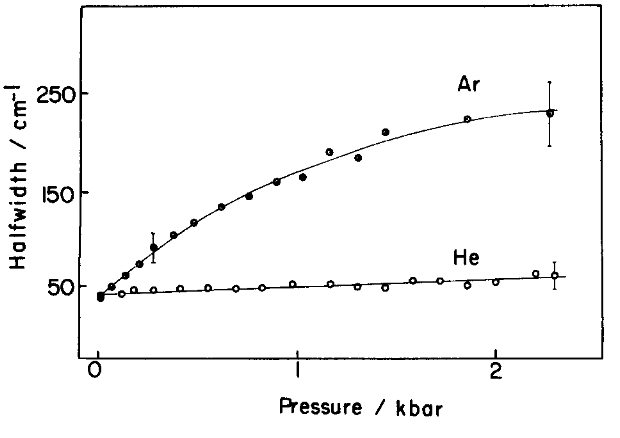

FIG. 7. Pressure dependences of the 6_0^1 band half-widths for benzene in argon (Ar) and in helium (He) at room temperature. The bandwidth of the benzene 6_0^1 band in argon at high pressures is obtained by a deconvolution of the overall contour shown in Fig. 1.

IV. DISCUSSION

A. Transition energy shifts

1. Comparison of theory and experiment

In our previous studies of the benzene/C_3H_8 [7] and benzene/N_2 [8] systems, liquid state theories of the solvent effect on solute electronic spectra have been satisfactorily applied for the calculation of the absorption energy shifts. In these references, both theory and experiment give a fairly linear dependence of the red energy shift on the experimental solution density. The present results of the energy shifts for the benzene/Ar and benzene/He systems are qualitatively different, thus suggesting that the existing theories may not be able to explain the observed spectroscopic behavior of benzene in argon and helium.

We consider the three theoretical models outlined in our previous report[7]: (1) the classical dielectric continuum model of Onsager and Böttcher (OB)[10,11]; (2) the microscopic dielectric model of Wertheim (W)[10,12]; and (3) the quantum statistical mechanical theory of Schweizer and Chandler (SC)[9]. For nonpolar solutions, dielectric models give explicit expressions for the solute absorption energy shift as a function of solvent dielectric constant (refractive index). The SC theory specifies the solute energy shift as a function of microscopic density and solute and solvent polarizabilities. For the explanation of specific theoretical expressions for the absorption energy shifts within the framework of each of the employed models the reader is referred to our previous paper[7] and references cited therein.

We recall briefly that the absorption energy shift ($\Delta\omega$) in OB theory is calculated using a simplified expression of the form

$$\Delta\omega = k\frac{(\epsilon - 1)}{(2\epsilon + 1)} \qquad (1)$$

in which ϵ is the density (temperature and pressure) dependent macroscopic static dielectric constant (for nonpolar systems) and k is a proportionality constant depending on the oscillator strength of the electronic transition considered and the solvent "cavity radius." Within the statistical microscopic approach of Wertheim $\Delta\omega$ is given by

$$\Delta\omega = 8k\xi \qquad (2)$$

in which the parameter ξ is related to the dielectric constant by

$$\epsilon = \frac{(1 + 4\xi)^2(1 + \xi)^4}{(1 - 2\xi)^6} \qquad (3)$$

and k is the same proportionality constant as in the OB model. Since calculation of the constant k would require specification of an arbitrary value of the cavity radius, the value of k is usually set to reproduce the known energy shift at particular experimental conditions. In order to reproduce the room temperature experimental transition energy shift for the benzene/Ar system at low densities, k has to be equal to 751 cm^{-1} for the OB model and 720 cm^{-1} for the W model. At higher densities (120 K and 130 K) of the liquid benzene/Ar solution, the OB model k values must be 441 and 536 cm^{-1}, respectively, in order to obtain reasonable agreement between calculations and experiment. The argon dielectric constant data used for calculation of the energy shifts in the dielectric models at room temperature are taken from Ref. 18. The experimental values of the dielectric constant of liquid argon at pressures up to 0.2 kbar are given in Ref. 19. At higher pressures the value of the dielectric constant is interpolated employing an empirically fit function of the Clausius–Mossotti form.[20]

The results of the calculations of the absorption energy shift as a function of solution density within the OB and W models for the benzene/Ar system are compared to the experimental values in Fig. 9. The energy shift in the fluid phase at low densities is well reproduced by the calculations. The calculated energy shift at high densities is too large in both models. Somewhat better agreement between the calculated energy shifts and the experimental results is obtained for benzene in the high density liquid phase of argon (using adjusted k values—see above), but the agreement is still not perfect; similar discrepancy between calculated and experimental energy shifts as reported for the fluid phase can be observed (see Fig. 9). The discrepancy in the liquid phase is not very pronounced since the experiments in liquid argon are performed within a relatively narrow range of densities. We are not able to perform experiments at higher densities in the liquid phase due to the solidification of argon. Generally, one can conclude that the dielectric OB and W models cannot reproduce the behavior of the energy shift for the benzene/Ar system observed at high densities. Moreover, dielectric models require the use of different constants k in order to fit the experimental values at different temperatures. This is an important limitation of the dielectric models.

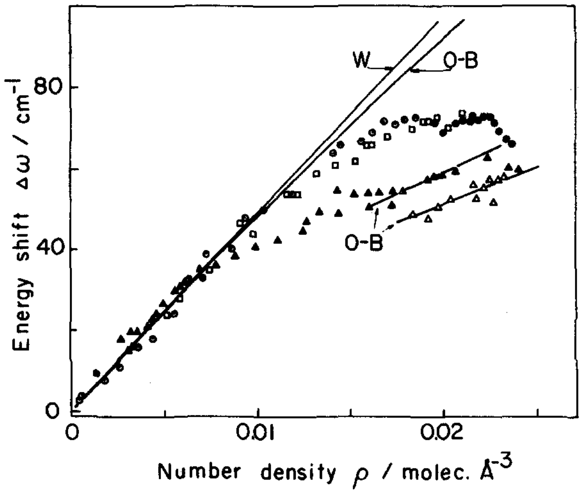

FIG. 9. Transition energy shift of the 6_0^1 band of benzene in argon as a function of number density. The experimental points are taken from Fig. 5. The lines represent the results of calculations for Onsager–Böttcher (OB), and Wertheim (W) models.

The quantum statistical mechanicl SC theory expresses absorption energy shift of a solute in an infinite solution as a function of normalized solvent reduced density ($\rho\sigma^3$), solute and solvent normalized molecular polarizabilities ($\alpha_{0,I}/\sigma^3$) and (α_0/σ^3), and solute and solvent absorption energies ($\omega_{0,I}/\omega_0$). The normalization factor σ is the hard sphere diameter of the solvent hard sphere liquid (fluid). The explicit expression for the absorption energy shift $\Gamma = \Delta\omega/\omega_{0,I}$ in the SC theory is given by[7,9]

$$\Gamma = \frac{2\pi^2 \dfrac{\alpha_{0,I} I_2^2(\rho\sigma^3) X}{\sigma^3 I_3(\rho\sigma^3) Y}\left\{1 - \left[1 - \dfrac{4\rho\sigma^3\alpha_0 I_3(\rho\sigma^3) Y}{\pi\sigma^3 I_2(\rho\sigma^3) X^2}\right]^{1/2}\right\}}{1 - \dfrac{X}{2Y}\left\{1 - \left[1 - \dfrac{4\rho\sigma^3\alpha_0 I_3(\rho\sigma^3) Y}{\pi\sigma^3 I_2(\rho\sigma^3) X^2}\right]^{1/2}\right\}},$$

with

$$X = (\omega_{0,I}/\omega_0)^2 - 1 + \frac{\alpha_0}{\sigma^3}\rho\sigma^3\frac{I_3(\rho\sigma^3)}{\pi I_2(\rho\sigma^3)},$$

$$Y = 8\pi^2\frac{\alpha_0 I_2^2(\rho\sigma^3)}{\sigma^3 I_3(\rho\sigma^3)},$$

in which the numerical functions $I_2(\rho\sigma^3)$ and $I_3(\rho\sigma^3)$ are given explicitly in Refs. 7 and 21. The specific values of the parameters used for the benzene/Ar system are as follows: ρ-variable experimental number density; $\alpha_{0,I} = 10.32$ Å^3 and $\alpha_0 = 1.64$ Å^3—the polarizabilities of benzene and argon taken from Ref. 22; $\omega_{0,I} = 38\,608$ cm^{-1}—the energy of the 6_0^1 benzene transition in the gas phase[2]; and ω_0—solvent absorption energy calculated from the first ionization of argon ($\hbar\omega_0 = 15.75$ eV).[23,24] The hard sphere diameter (σ) is slightly temperature and pressure dependent and is calculated within the approach of the WCA theory[25,26] at each particular temperature and pressure using the iterative procedure given by Verlet and Weis.[27] Although the SC theory does not explicitly include the temperature effect on the transition energy shifts at constant density, inclusion of the temperature dependence of the hard sphere diameter indirectly accounts for some change in energy shift with temperature. The parameters of the argon Lennard-Jones potential used in the calculations of σ are[22] $\sigma_{LJ} = 3.405$ Å and $\epsilon/k_B = 119.8$ K. As can be seen in Fig. 10(a), σ is a weakly decreasing function of temperature. This result agrees with physical expectations since due to the increase of the kinetic energy with temperature the molecules can approach closer during collisions.[28] The calculated density dependence of σ [see Fig. 10(b)] is nearly negligible at low densities but is more important at high densities. Similar temperature and density dependences of the hard sphere diameter can be obtained for helium and nitrogen.

The results of the calculations of the absorption energy shift Γ for the benzene/Ar system within the SC theory are compared to the experimental data in Fig. 11. As predicted by the authors of the theory the calculated absolute energy shift is an order of magnitude too large compared to the experimental values. Similar discrepancies have also been reported for benzene/C_3H_8 [7] and benzene/N_2 [8] systems and are presumably due to the simplifying assumptions of the theory, such as use of the two parameter harmonic oscillator (Drude) model and the neglect of interactions between the observed electronic transition and the many other solute and solvent electronic transitions with various oscillator strengths. For the above reasons we follow Schweizer and Chandler and compare experimental and calculated relative energy shifts expressed as Γ/Γ_0. Such a comparison (see Fig. 12) gives good agreement between the calculated and experimental relative energy shifts again only at low densities. At high densities, theory predicts energy shifts much greater than those observed experimentally, just as found for the dielectric models. Note (Fig. 11) that the inclusion of the temperature and density dependences of the hard sphere diameter does not qualitatively change the behavior of the energy shifts. Slightly smaller absolute energy shifts are calculated at low temperatures (at a constant density), in agreement with the trend observed experimentally. As noted above, this trend is only a minor effect and has little to do with the comparison of theory with experiment in the Γ/Γ_0 coordinate (Fig. 12).

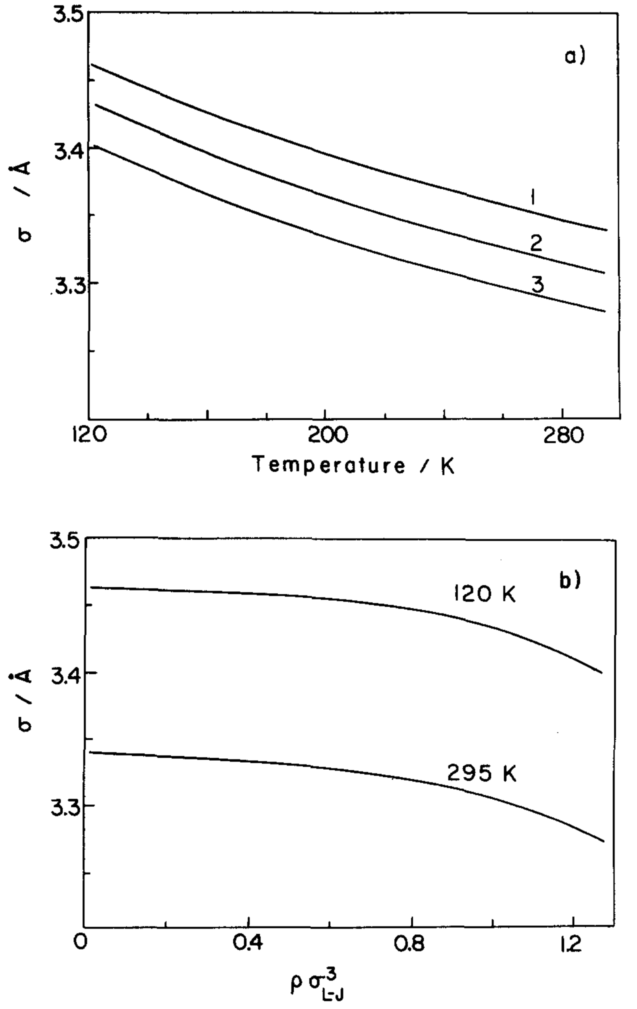

FIG. 10. Temperature (a) and density (b) dependences of the hard sphere diameter for argon calculated according to the procedure given in Ref. 27. The temperature dependences are calculated at densities $\rho\sigma^3_{LJ}$ equal to: (1) 0.1; (2) 1.0; and (3) 1.25.

The above results clearly demonstrate that neither the dielectric nor microscopic quantum mechanical theories can explain the spectroscopic behavior of the benzene/Ar system at high densities. Similar conclusions can be reached for benzene/He, since for this system dielectric and quantum statistical mechanical models would predict only a small red energy shift with increasing density, whereas blue energy shifts are observed. The explanation of the failure of theoretical predictions of energy shifts in benzene/Ar and benzene/He systems is discussed below.

2. Qualitative explanation of energy shifts—comparison between the benzene/N_2, benzene/Ar and benzene/He system

The dominance of attractive dispersion interactions in the intermolecular potential typically causes solution electronic transitions to be red shifted with respect to their gas

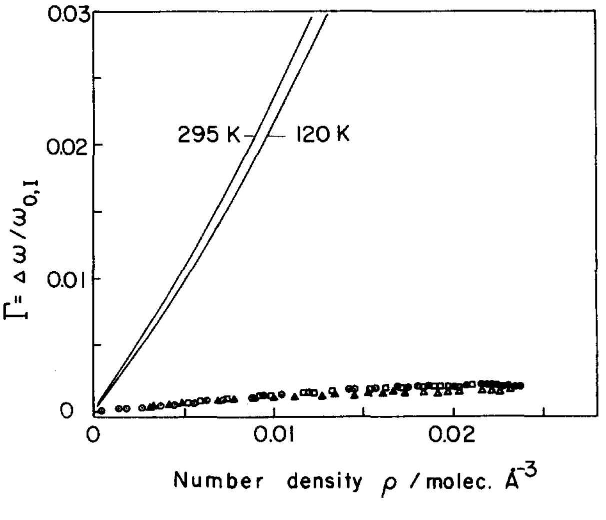

FIG. 11. Energy shift Γ of the 6_0^1 band of benzene in argon as a function of the number density. The experimental points correspond to those in Figs. 3–5. The lines represent results of calculations of the SC theory at two different temperatures, with the inclusion of the temperature and density dependence of the hard sphere diameter.

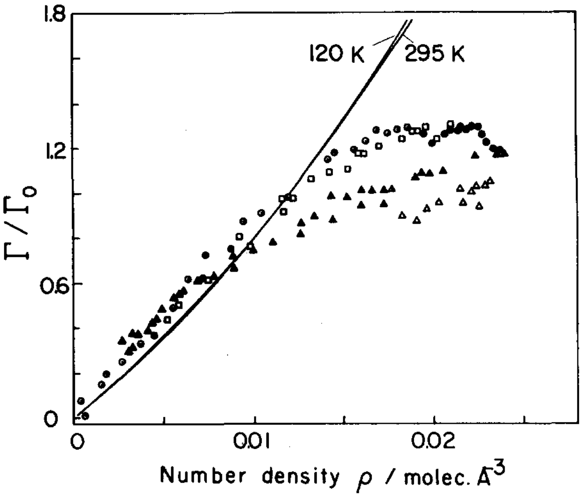

FIG. 12. Relative energy shift Γ/Γ_0 of the 6_0^1 absorption band of benzene in argon as a function of the number density. Different experimental points correspond to dependences depicted in Figs. 3–5. The lines are calculated according to the SC theory as in Fig. 11.

phase values, while the dominance of repulsive interactions in the intermolecular potential typically causes these solution transitions to undergo blue shifts. The former case is apparently observed for the benzene/N_2 solution, whereas the latter case is observed for the benzene/He solution. Blue energy shifts for electronic transitions have also been reported for the Xe/Ar system[15] and have been explained by taking into account the repulsive interactions.

We believe that the adoption of point dipoles (dispersion interactions) and neglect of the explicitly repulsive coupling due to charge overlap of extended electronic distributions are the main reasons for the failure of the theory to describe the energy shifts in the benzene/Ar and benzene/He systems. The differences in behavior between the benzene/N_2, benzene/Ar, and benzene/He systems can be rationalized as follows:

(a) The molecular polarizabilities of the three solvents (see Table I) are in the order $\alpha(N_2) > \alpha(\mathrm{Ar}) \gg \alpha(\mathrm{He})$. Thus, dispersion interactions are larger in N_2 then in Ar or He. Consequently, one would expect repulsive interactions to become more important in He and Ar than in N_2 at comparable high densities.

Moreover, effective atomic polarizabilities of the noble gases decrease with increasing reduced density: for example, for argon[29]

$$\alpha = \alpha_0(1 - 0.004\rho\sigma^3 - 0.02(\rho\sigma^3)^3 + \cdots).$$

This effect, although small, further reduces the importance of the attractive interactions at high densities.

(b) As a consequence of differences in dispersive forces and molecular size, the number density of the three solvents is in the order $\rho(\mathrm{He}) \gg \rho(\mathrm{Ar}) > \rho(N_2)$ at constant temperature and pressure. Thus the intermolecular distances are in the order $R(N_2) > R(\mathrm{Ar}) \gg R(\mathrm{He})$ and the relative repulsion contribution to the intermolecular potential are in the order $V_{\mathrm{rep}}(\mathrm{He}) \gg V_{\mathrm{rep}}(\mathrm{Ar}) > V_{\mathrm{rep}}(N_2)$.

A density dependent competition between repulsive and attractive interactions always exists in solutions. At high density, the repulsive part of the potential becomes more important for the overall fluid equilibrium and thus red shifts tend to decrease and blue shifts tend to increase at high pressures (densities). The benzene/N_2 system has a small repulsive term and a large attractive term at the densities employed here and thus displays a fairly linear and normal (red shifted) behavior. The benzene/Ar system has a more nearly equal balance of repulsion and attraction throughout the range of accessed densities and thus only smaller red shifts are observed with increasing density and pressure. The benzene/He system has dominant repulsion terms which always increase the blue shift of the benzene 6_0^1 transition as pressure (density) is increased.

These arguments would suggest that at higher densities than those reached in our work the benzene/N_2 and benzene/C_3H_8 systems studied previously[7,8] would also show deviations from linear red shifts with density.

Both dielectric and microscopic theories are essentially based on the hard sphere approximation and Coulomb interactions, specifically, only point dipoles and dispersive interactions are explicitly included. This approach leads generally to the prediction of a red transition energy shift, since the excited state polarizability of the solute molecule is typically larger than the ground state polarizability, and the energy shift results from the difference in energy in the ground and excited states. The SC theory can, in principle, predict blue energy shifts in the case of polar solutes (if the permanent dipole moment changes significantly upon excitation from the ground to the excited state), but clearly this is not applicable to He, Ar, N_2, or C_3H_8. Explicit inclusion of the short range repulsive interactions into the microscopic solvent shift theory should improve the agreement between the theoretical calculations and experiments presented here: basically the spherical molecule and point dipole approximations

TABLE I. Comparison of selected molecular parameters for helium, argon, and nitrogen.

	σ_{LJ}[a] (Å)	ϵ/k_B[a] (K)	σ[b] (Å)	Mass (g)	Polarizability α (Å^3)	Dispersion energy coefficient[a] (erg cm^6)
He	2.556	10.22	2.328	4.0026	0.2049	1.29
Ar	3.405	119.8	3.340	39.948	1.64	109.2
N_2	3.698	95.05	3.569	28.013	1.76	125.6

[a] Data taken from Ref. 22 in the Lennard-Jones form.
[b] Room temperature values.

are not necessarily valid. Unfortunately, this is not an easy task, since the short range repulsive interactions depend on particle packing and the details of molecular shape.

B. Linewidths

Linewidths cannot be calculated by either the dielectric or quantum statistical mechanical models of solutions. The inability of the SC theory to generate a half-width dependence on density is a limitation imposed by the mean field nature of the theory and the adoption of the harmonic oscillator model for the fluctuating dipoles. Therefore, only a qualitative explanation of bandwidth changes with temperatures and pressure can be offered.

The broadening of vibrational bands as a function of pressure can be primarily ascribed to so called "pressure broadening" resulting from the perturbations of the energy levels by fluctuations of the intermolecular forces.[30] In gases, pressure broadening increases rapidly with density and the rate of inelastic collisions giving the dominant contribution to the linewidths at high pressures. Broadening of vibrational bands can be also caused by quasielastic collisions leading to a phase shift in the molecular wave function without changing the molecular energy levels. Although these two processes, energy relaxation and dephasing, were initially postulated for the gaseous state, in which collision processes are well defined and isolated, their extension to dense fluids and liquids has proven to be very useful.

In the experiments presented here, the broadening of the vibronic transition bands with pressure (see Fig. 7) is much larger than those usually observed for vibrational bands and can be due to the changes in the shape of the intermolecular potential. Most probably perturbation of the electronic state itself with increase of pressure entirely accounts for the band broadening.

Such a perturbation of benzene electronic states should be much more pronounced for argon and nitrogen solutions than for helium solutions for two reasons: (1) helium has weak intermolecular attractive interactions due to its small size and polarizability; and (2) collision-induced perturbations in the case of helium solutions are small because the helium has a small mass, a large diffusion rate and a short collision time.

Broadening of the absorption features with increasing temperature is similar for argon and helium solutions at relatively low pressures (see Fig. 8), and is presumably due to the changes in the thermal equilibrium population of states. At high pressures (densities) the broadening of benzene vibronic features in argon solutions with increasing temperature is more pronounced, probably because the attractive part of the benzene/Ar intermolecular potential becomes steeper at high densities. This effect is not pronounced in the benzene/He system because of weak attractive interactions and slowly varying attractive part of the potential.

Finally, one should note that broadening of the 6_0^1 band of benzene in argon takes place toward the low energy side of the spectrum. This effect can be qualitatively explained by the fact that the attractive part of the excited state potential accessed by absorption is asymmetric and becomes steeper at higher densities (pressures).[7,8]

V. CONCLUSIONS

Optical absorption spectra of the ${}^1B_{2u} \leftarrow {}^1A_{1g}$ electronic transition of benzene dissolved in argon (fluid and liquid) and helium (fluid) are studied as a function of pressure, temperature, and density. The experimental results can be summarized as follows:

(1) Red energy shift of the benzene absorption spectrum in argon solutions is observed with increasing pressure at constant temperature, and with decreasing temperature at a constant pressure; that is, with increasing density. In fluid argon, the energy shift is a linear function of density at low densities. At high densities, in both fluid and liquid phases, density dependent reduction of the red energy shift is found; at densities of ~ 0.022 molecule/Å^3 almost no further energy shift is observed. Therefore, the behavior of the transition energy shifts in the benzene/Ar solution is different from that found for benzene/N_2 and benzene/C_3H_8 systems, in which the energy shift is linear function of density within the whole investigated density (pressure) range.

(2) As reported for the benzene/N_2 solution, the density dependence of the transition energy shift for benzene/Ar exhibits a small "thermal hysteresis" at relatively high densities. This indicates that apart from the density effect on the energy shifts, an additional small temperature effect has to be taken into account. This effect is most probably due to the changes in the equilibrium thermal population of intermolecular energy levels.

(3) Blue transition energy shifts for the benzene/He solution are observed with increasing pressure at room temperature, and with decreasing temperature at a constant pressure; that is, with increasing density. The energy shift is a weak linear function of density at low densities and a greater than linear function at high densities. The behavior of the benzene/He solution is thus completely different than that found for the benzene/Ar and benzene/N_2 solutions, most probably due to the predominance of repulsive interactions and lack of substantial attractive interactions.

(4) Broadening of the absorption bands with increase of both pressure and temperature is found for benzene/Ar solutions; a similar broadening of the bands, due to both changes in the solute/solvent intermolecular potential and thermal population of states, was previously reported for benzene/N_2 and benzene/C_3H_8 solutions.

(5) No comparable broadening of the benzene spectral features is found in fluid helium. The lack of band broadening in the benzene/He system is ascribed to weak attractive interactions and "flatness" of the attractive part of the potential accessed in absorption. The reduced importance of collisional broadening effects can also contribute to the difference between He and the other solvents.

The experimental results for the absorption energy shifts for the benzene/Ar system are compared to the theoretical calculations of the dielectric Onsager–Böttcher (OB) and Wertheim (W) models, as well as to the quantum statistical mechanical theory of Schweizer–Chandler (SC). The results can be outlined as follows:

(1) All three models employed for the calculations of the energy shifts for the benzene/Ar system reproduce fairly well the linear dependence of the energy shift at low densities

in the fluid phase. Nonetheless, the theory fails to describe the energy shifts at high densities, predicting larger shifts than experimentally observed.

(2) Additional inclusion of the temperature and pressure dependences of the hard sphere diameter into the calculations of the transition energy shifts within the framework of the SC theory does not improve agreement between theory and experiment. At constant density the absolute calculated energy shift is a weakly increasing function of temperature in agreement with the experimental observations.

(3) Comparison of the energy shifts for the benzene/Ar system at low densities (in the linear part of the energy/density dependence) with previously reported data for the benzene/N_2 and benzene/C_3H_8 systems, supports the prediction of the SC theory that the energy shift is an increasing function of polarizability. This comparison can be made only under conditions in which attractive interactions prevail.

(4) All three theories predict small red energy shifts for benzene/He solutions contrary to the experimental observation of the energy shift to the blue.

(5) Failure of the employed theories to described absorption energy shifts in benzene/Ar system at high densities, as well as in benzene/He system is ascribed to the neglect of strong density dependent repulsive interactions. Only long range dispersive interactions between induced molecular point dipoles are explicitly considered in the theoretical description of the energy shifts.

Finally, we note that fluid argon is generally similar to fluid nitrogen in terms of the Lennard-Jones potential, molecular polarizability, and other physical properties. Therefore, at densities high enough to reduce considerably the attractive interactions and increase the repulsions, one may expect that the energy shift for the benzene/N_2 solution will also become nonlinear function of solution density. Such an effect, however, has not been observed in our experiments at pressures up to 3 kbar.

ACKNOWLEDGMENTS

We thank Professor B. M. Ladanyi for critical reading of the manuscript and helpful discussions concerning the implementation of the temperature and density dependences of the hard sphere diameter into the theory. Dr. W. M. Haynes (NBS-Boulder, CO) provided us with thermodynamic data for argon and helium.

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