Spectroscopic studies of cryogenic fluids: Benzene in nitrogen

R. Nowak and E. R. Bernstein

Citation: The Journal of Chemical Physics **86**, 4783 (1987); doi: 10.1063/1.452700
View online: http://dx.doi.org/10.1063/1.452700
View Table of Contents: http://aip.scitation.org/toc/jcp/86/9
Published by the American Institute of Physics

Spectroscopic studies of cryogenic fluids: Benzene in nitrogen[a)]

R. Nowak[b)] and E. R. Bernstein
Department of Chemistry, Condensed Matter Sciences Laboratory, Colorado State University, Fort Collins, Colorado 80523

(Received 8 January 1987; accepted 28 January 1987)

Energy shifts and bandwidths for the ${}^1B_{2u} \leftarrow {}^1A_{1g}$ optical absorption of benzene in supercritical nitrogen are presented as a function of pressure, temperature, and density. The pressure and density dependence of energy shifts of room temperature emission of benzene in nitrogen fluid is also reported. Both absorption and emission spectra exhibit shifts to lower energy as a function of density, whereas almost no spectral shifts are observed if the density is kept constant and temperature and pressure varied simultaneously. Thus, density is the fundamental microscopic parameter for energy shifts of optical transitions in supercritical nitrogen. This result is analogous to the findings for the liquid benzene/propane system and can be interpreted qualitatively in terms of changes occurring in the intermolecular potential; however, in the benzene/supercritical nitrogen system an additional small density independent temperature effect on the transition energy has been identified. Experimental results are compared to dielectric (Onsager–Böttcher and Wertheim) and microscopic quantum statistical mechanical (Schweizer–Chandler) theories of solvent effects on solute electronic spectra. Reasonably good agreement between experiment and theory is found. The results demonstrate that liquid state theory can be used to describe the supercritical nitrogen fluid.

I. INTRODUCTION

Optical spectroscopic studies of aromatic solute molecules in simple cryogenic liquids have been used to elucidate such microscopic properties of liquid solutions as intermolecular interaction potentials[1,2] and liquid state dynamics.[2–4] Studies of optical spectra as a function of density, temperature, and pressure are important for experimental verification of theories of solvent effects on solute electronic spectra because density is an important parameter in microscopic theories.[5] Cryogenic liquids are generally well suited for such studies of the liquid phase because they have proven to be good solvents for simple aromatic molecules, and yield well resolved (for the liquid state) low temperature spectra of solutes.[1–4,6,7] Moreover, due to their relatively low critical temperatures, many cryogenic systems can be, in principle, studied spectroscopically in their supercritical fluid phase, provided that well resolved spectra are found. Such a study is of great interest since little spectroscopic data have been reported for supercritical phases.

We have recently studied absorption and emission of benzene dissolved in liquid propane as a function of density (both temperature and pressure).[8] The results of transition energy shifts were compared to dielectric[9–11] and quantum statistical mechanical[5] theories of solvent effects on solute electronic spectra and interpreted qualitatively in terms of changes occurring in the intermolecular potentials for the ground and excited states of the solute.

The main goal of the present paper is to describe and interpret the spectroscopic behavior of benzene in supercritical nitrogen fluid. Absorption energy shifts and bandwidths of the benzene ${}^1B_{2u} \leftarrow {}^1A_{1g}$ transition are determined as a function of pressure and temperature (density) and room temperature emission is studied as a function of pressure. The comparison of the experimental data with the dielectric models of Onsager–Böttcher[9,10] (OB) and Wertheim[9,11] (W) and with microscopic theory of Schweizer and Chandler[5] (SC) shows that the theory of the liquid phase can be satisfactorily applied to the supercritical phase of nitrogen. Specifically, the theory is found to reproduce quite well the relative energy shifts of the benzene absorption spectrum as a function of microscopic density. In terms of energy shifts the spectroscopic behavior of benzene in supercritical nitrogen is very similar to that in liquid propane.[8]

II. EXPERIMENTAL PROCEDURES

The experimental setup is analogous to the one described elsewhere.[7,8] A UV xenon lamp and pulsed Nd^{+3}/YAG pumped dye (LDS 698) laser (frequency doubled and mixed with the 1.064 μm fundamental) are used as light sources for absorption and emission, respectively. Absorption spectra are recorded with a photon counting system and a 1 m monochromator. Emission spectra are dispersed with the same monochromator and recorded with a boxcar averager.

The sample is maintained at the desired pressure and temperature in a 1 cm^3 volume and a 1.2 cm absorption pathlength high pressure cell. The cell and pressurizing system are described in more detail in Ref. 8. High pressure is measured with an accuracy ± 20 bar with resistance pressure transducers. Sample temperature is stabilized with a mechanical helium refrigerator.

Commercial high purity benzene and nitrogen are used without additional purification. Gas samples are prepared at room temperature by mixing known amounts of solute and solvent. Benzene concentration is typically 50–400 ppm and varies with both temperature and pressure. Additionally, the

---

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

[b)] On leave from the Institute of Organic and Physical Chemistry, Technical University of Wrocław, 50-370 Wrocław, Poland.

0021-9606/87/094783-07$02.10

number of benzene molecules in the optical path changes with solution density. These changes are not important for the interpretation of transition energy shifts and transition half-widths. Transition energies are measured with an absolute error of ~ 20 cm^{-1}, depending on the bandwidth (temperature and pressure). The relative transition energy shifts are determined to within an accuracy of better than 10 cm^{-1}.

III. RESULTS AND DISCUSSION

A. Experimental findings

The intense vibronically induced series $6_0^1 1_0^n$ ($n = 0,1,2,3,...$) of the benzene $^1B_{2u} \leftarrow {}^1A_{1g}$ electronic transition is studied as a function of pressure, temperature, and density in the ranges 0–3 kbar, 150–295 K, and 0–900 kg m^{-3}. The energy shifts of the absorption bands are determined at constant temperature and variable pressure, constant pressure and variable temperature, and constant density (simultaneously variable temperature and pressure). Dispersed emission spectra of the corresponding emission transition ($6_1^0 1_n^0$) are determined at room temperature and pressures up to 1.5 kbar. At higher pressure, emission intensity decreases drastically due to an efficient quenching of fluorescence. The $^1B_{2u}$ state of benzene may relax through a high-efficiency nonradiative pathway accessible at energies ~2500 cm^{-1} above the zero point energy of the $^1B_{2u}$ state.[12,13] Other nonradiative decay channels (e.g., intersystem crossing) may additionally be open at room temperature and high pressure. Emission spectra at low temperatures are not measured due to experimental difficulties caused by the reduced solubility of benzene in nitrogen at low temperatures. As all the bands in the spectra exhibit similar energy shifts and broadening as a function of pressure and temperature, only the representative behavior of the 6_0^1 and 6_1^0 bands is discussed.

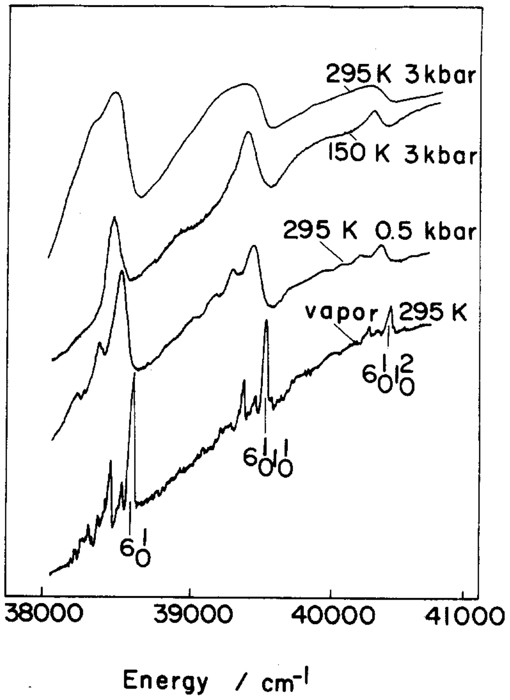

FIG. 1. Typical pressure and temperature development of the $^1B_{2u} \leftarrow {}^1A_{1g}$ absorption spectrum of ~200 ppm of benzene in nitrogen.

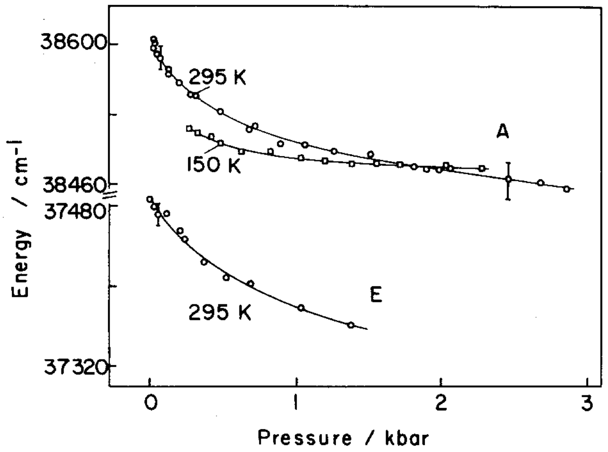

FIG. 2. Pressure dependences of the benzene 6_0^1 and 6_1^0 band energies for absorption (A) and emission (E). Emission is not studied at higher pressure due to the decrease of emission intensity with increasing pressure. Absorption data are given at 295 K (○) and 150 K (□).

Typical pressure and temperature development of the absorption spectrum of benzene is shown in Fig. 1. Red energy shifts of the spectra and pronounced band broadening with increasing pressure at constant temperature are observed. The pressure dependence of the energy shifts is summarized in Fig. 2. Both absorption and emission spectra are red shifted with increasing pressure at a constant temperature; that is, with an increase in isothermal density. The pressure dependence for emission seems to be slightly steeper than the corresponding dependence for absorption, but the magnitude of this difference is small. Similar room temperature absorption energy shifts of benzene in nitrogen have been reported in the literature[14–16]; however, no sound theoretical interpretation and detailed analysis of the shift were offered.

As can be seen in Fig. 2, the pressure dependence for the absorption energy shift varies with temperature. This trend is presumably caused by the pressure and temperature dependence of density. Temperature dependence of the energy

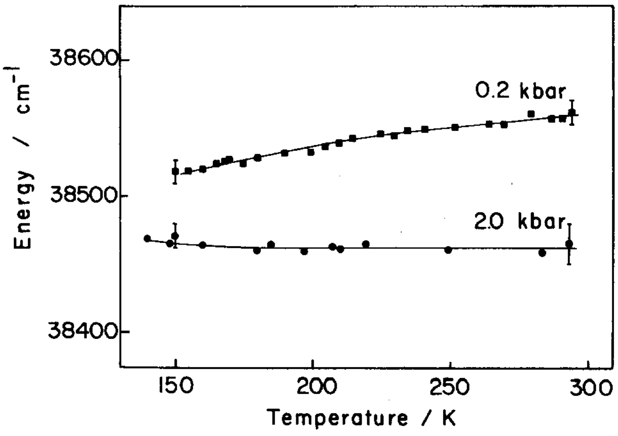

FIG. 3. Temperature dependences of the benzene 6_0^1 absorption band taken at two pressures: 0.2 kbar (■) and 2.0 kbar (●).

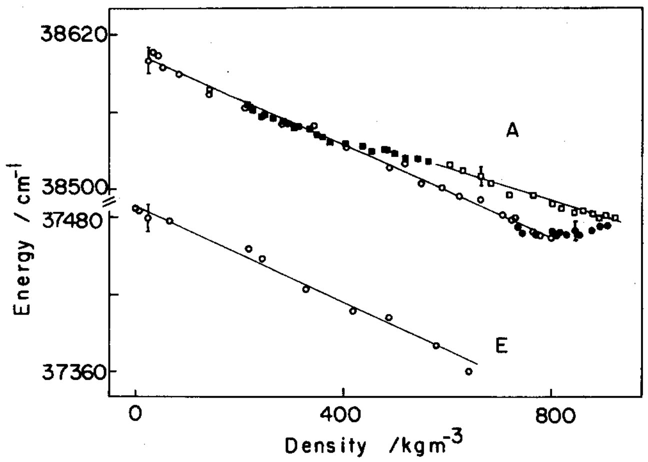

FIG. 4. Absorption (A) and emission (E) band energy from Figs. 2 and 3 plotted as a function of experimental density calculated from thermodynamic data. Different points correspond to the experimental runs given in the above figures. The lines serve only as a guide for the eye.

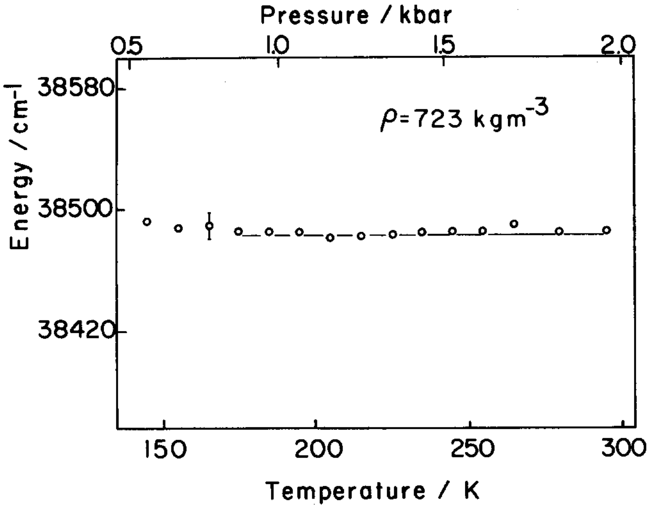

FIG. 5. The 6_0^1 absorption band energy measured at constant density $\rho = 723$ kg m^{-3} as a function of simultaneously varied temperature and pressure. Deflection from a flat linear dependence can be seen at low temperatures.

shift for absorption is shown in Fig. 3. The absorption spectrum shifts to the red with decreasing temperature at low constant pressure (0.2 kbar) but at pressures as high as 2 kbar no energy shift larger than the experimental error is observed. Again this observation can be partially explained by the temperature and pressure dependence of the fluid density[17] and will be discussed below.

Both constant temperature variable pressure and constant pressure variable temperature dependences from Figs. 2 and 3 can be expressed as a function of the experimental density calculated from thermodynamic data.[17] Plots of energy shifts as a function of density given in Fig. 4 show that the energy shift for both absorption and emission is a linear function of density. The slope of this dependence for absorption varies from ~ 17 cm^{-1}/100 kg m^{-3} at room temperature to ~ 14 cm^{-1}/100 kg m^{-3} at 150 K. As a result the transition energy measured at low temperatures and high densities is slightly higher (up to 20 cm^{-1}) than the transition energy measured at room temperature at the same density. The transition energy shift (Fig. 4) obtained by decreasing the temperature at a constant low pressure (data from Fig. 3) is also smaller than the pressure induced room temperature shift in the same range of densities. This result indicates that changes in density cannot entirely account for the observed energy shift; the energy shift is not only a function of solution density but also depends on the large change in thermal population of states between 150 K and room temperature. This temperature effect on the energy shifts seems to be particularly important at high densities (pressures). The constant high pressure (2 kbar) variable temperature energy shift dependence (see Fig. 3) indicates that the expected red shift of ~ 25 cm^{-1} due to ~ 160 kg m^{-3} change in density (corresponding to a temperature variation between 150 and 295 K) is entirely canceled most probably by the opposite effect due to the change in thermal population of states.

The finding that the transition energy shift is for the most part a linear function of density suggests that the density dependent intermolecular distance is an important microscopic parameter governing the solute spectral shift, even though the small temperature effect on the transition energy shifts cannot be completely neglected as discussed above. If density is the fundamental microscopic parameter, spectra taken at constant density (variable pressure and temperature) should evidence little change in energy due to the temperature (kinetic) effect. Absorption spectra taken at constant density do not exhibit pronounced energy shifts within large variations of temperature and pressure: only a small constant density (Fig. 5) shift of the transition energy is observed below ~ 200 K. Since the considered constant density (temperature) shift is of the order of experimental uncertainty, this effect cannot be quantitatively isolated and well characterized. This result demonstrates the fundamental nature of density for the spectroscopic behavior of benzene in supercritical nitrogen.

Analogous findings for the benzene/propane liquid system have been reported.[8] Due to a low solubility of benzene in nitrogen at temperatures below $T_c = 126.26$ K (i.e., in the liquid phase), we are not able to perform high pressure spectroscopic experiments in liquid nitrogen. The similarity of spectroscopic behavior for the supercritical benzene/nitrogen and liquid benzene/propane[8] systems nonetheless suggests that the qualitative explanation of both sets of experiments should be the same. Specifically, the similar transition energy shifts for both absorption and emission are mostly due to the relative change of the energy gap between the ground and excited state potentials as given in Ref. 8.

Temperature and pressure dependences of the bandwidths are presented in Figs. 6 and 7. Absorption halfwidths increase with both increasing temperature and pressure. The room temperature gas phase spectrum of benzene in nitrogen at ~ 1 atm is characterized by sharp features but can be gradually transformed in to a broad spectrum by increasing the pressure (see Fig. 1). This effect has already been reported.[18] Broadening and rounding of the spectral features are due to a very large change of density (collision

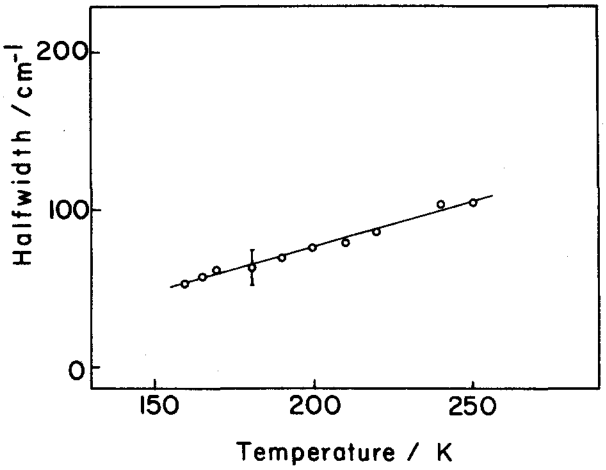

FIG. 6. Temperature dependence of the absorption 6_0^1 band half-width at pressure 0.2 kbar.

rate) and intermolecular distance with increasing pressure. Intermolecular relaxation is also associated with and enhanced by increased density and may well contribute to the overall linewidth. Similar, although less pronounced, broadening of the absorption features with increase of pressure in the benzene/propane system has been explained by the "narrowing" of the intermolecular potential well.[8] At high pressure the attractive part of the potential is presumably steeper, thus a larger portion of the intermolecular potential can be accessed by absorption, leading to band broadening.

In supercritical nitrogen the benzene absorption bands broaden with increasing temperature at low pressure (see Fig. 6). This change in bandwidth with increasing temperature is not found in the liquid propane/benzene system.[8] Two effects can be responsible for this broadening: changes in the equilibrium thermal population of states and changes occurring in the intermolecular potential due to a decrease in density with increasing temperature. The latter effect would be much less pronounced in liquid propane (at low pressures) due to the considerably smaller changes of density in the liquid phase with increasing temperature as compared to supercritical phase. These two effects can be separated by measuring bandwidths at constant density. The increase in bandwidth measured at constant nitrogen density ($\rho = 723$ kg m^{-3}), generated by simultaneously varying temperature (160–250 K) and pressure (0.7–1.6 kbar) is ~ 35 cm^{-1} over this range. Thus, clearly both the population of inter- and intramolecular energy levels and intermolecular distances and collisions (density) play an important role in determining the absorption bandwidths in the benzene/nitrogen supercritical fluid system.

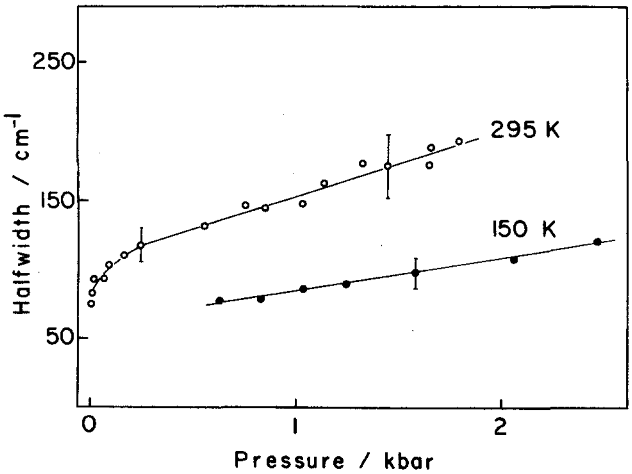

FIG. 7. Pressure dependences of the absorption 6_0^1 band half-width at room temperature and 150 K.

Finally, note that broadening of the absorption transition takes place mostly to the low energy side of the features (see Fig. 1). This is consistent with previous findings[1,2] that the excited state intermolecular potential minimum lies at a smaller intermolecular solute/solvent separation than does the ground state potential minimum.

B. Comparison between liquid state theory and experiment

The experimental results demonstrate that the spectroscopic behavior of benzene in supercritical fluid nitrogen resembles qualitatively the behavior of benzene in liquid propane.[8] This finding suggests that liquid state theories of solvent effects on solute electronic spectra can be, in principle, applied to supercritical fluids, at least in the region of high liquid-like density. We consider the three most often used theoretical models outlined in our previous paper[8]: the continuum dielectric Onsager–Böttcher (OB) model[9,10]; the dielectric statistical model of Wertheim (W)[9,11]; and microscopic quantum statistical mechanical theory of Schweizer and Chandler (SC).[5] The former two models specify solute absorption energy shift in terms of a density and temperature dependent solvent dielectric constant (refractive index). The latter theory expresses the energy shift as a function of microscopic density and solute and solvent polarizabilities. Since the calculations presented here are analogous to those performed for the benzene/propane system, the reader is referred to our prevous paper[8] for specific theoretical expressions and their explanation.

Within the framework of dielectric theories,[9] absorption energy shifts are calculated using Eq. (5) of Ref. 8 for the OB model and Eqs. (4) and (6) for the W model. The solute dependent proportionality constant k is set to reproduce the experimental benzene transition energy shift between the vapor and high density supercritical nitrogen fluid phase at both room temperature and 150 K. Density and density dependent dielectric constant data for nitrogen at different experimental temperatures and pressures are taken from Ref. 17.

The results of calculations of the energy shift using OB and W models are compared to the experimental results in Fig. 8. In order to reproduce the room temperature data k is chosen to be 1305 cm^{-1} for OB model and 1234 cm^{-1} for W model. Since both calculations give almost identical dependence only one calculated line is shown for room temperature data in Fig. 8. At 150 K the results are fit with $k = 1080$ cm^{-1} and $k = 1034$ cm^{-1} for OB and W models, respectively. The data obtained by temperature variation (at 0.2 kbar) plotted in the same figure can be fit analogously using

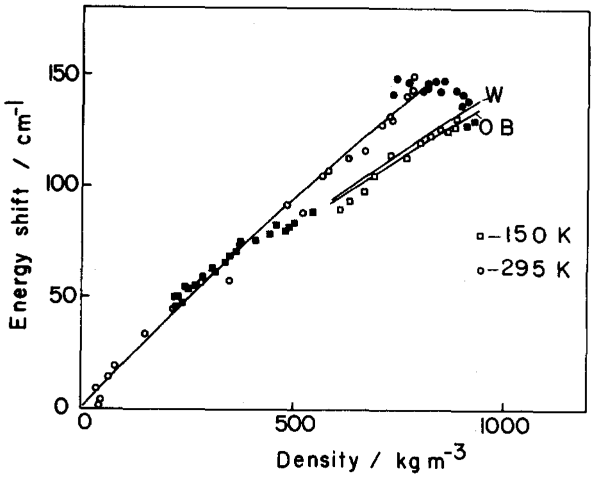

FIG. 8. The 6_0^1 absorption band energy shift as a function of solution density. Experimental points correspond to those from Figs. 2 and 3. The lines are calculated using OB and W models taking into account density (temperature and pressure) dependence of the dielectric constant. The values of the "fitting constant" k are derived to give the best fit.

$k = 1330$ cm^{-1} for OB and $k = 1269$ cm^{-1} for W model; however, the plot is good only for relatively low densities (high temperatures). As can be seen, the absorption energy shift can be in general described employing a density (both pressure and temperature) dependent dielectric constant. Different specific values of the proportionality constant k must be used at different temperatures, since neither OB nor W models include temperature effects.

The microscopic SC theory[5] expresses absorption energy shifts as a function of microscopic density (ρ), solute and solvent isolated molecule polarizabilities ($\alpha_{0,I}$ and α_0), and solute and solvent absorption band frequencies ($\omega_{0,I}$ and ω_0). The explicit expression is given by Eq. (14) of Ref. 8. The specific values of the parameters used for calculations are chosen as follows: ρ—variable experimental nitrogen density calculated as the number of molecules per unit volume; $\alpha_{0,I} = 10.32$ Å^3 and $\alpha_0 = 1.76$ Å^3 are taken from Ref. 19; $\omega_{0,I} = 38\,608$ cm^{-1} is the benzene gas phase energy of the 6_0^1 transition; and $\omega_0 = 790\,452$ cm^{-1} is nitrogen electronic transition energy calculated from the value of the first ionization energy ($\hbar\omega_0 = 15.6$ eV).[20] The hard sphere diameter for the nitrogen hard sphere fluid ($\sigma = 3.678$ Å) is calculated according to the WSA theory[21] using the iterative procedure given in Ref. 22. A constant value of σ is used at all temperatures and pressures. Such an approximation is justified because the hard sphere diameter is in general only a weak function of temperature and almost pressure independent.[22,23] Inclusion of the temperature and pressure dependences of σ has only a minor effect (negligible compared to the experimental uncertainty) on the slope of calculated relative energy shifts in SC coordinates.[23]

The result of the calculation of the relative energy shift $\Gamma = (\omega - \omega_{0,I})/\omega_{0,I}$ as a function of normalized density is compared to the experimental results in Fig. 9. The calculations of the SC theory reproduce explicitly the experimental results faithfully although, again, the theory does not include the previously discussed temperature variation of the absorption at constant density. The calculated relative energy shift is a slightly stronger (nonlinear) function of density than experimentally observed.

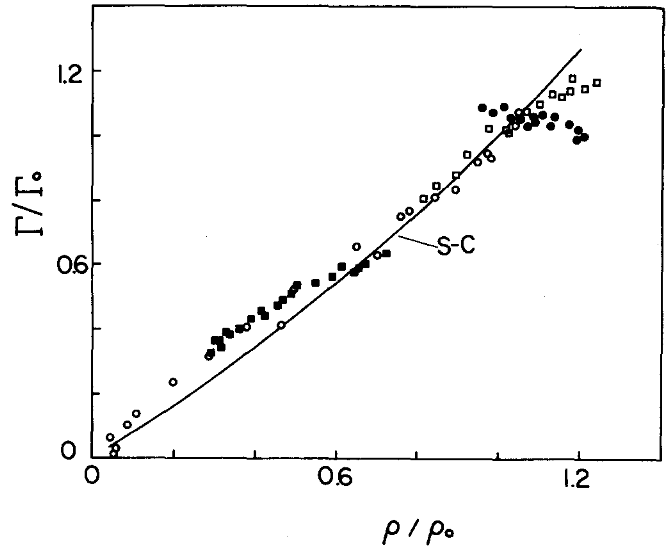

FIG. 9. Relative shift of the absorption 6_0^1 band as a function of normalized density. Γ_0 is a relative energy shift at a density $\rho_0 = 750$ kg m^{-3} corresponding to an average density of nitrogen liquid phase (liquid density varies between ~500 and 1050 kg m^{-3} depending on temperature and pressure). Differently marked points stand for various experimental runs in different density regions analogously to Figs. 2 and 3. The line represents the results of calculations for the Schweizer–Chandler (SC) model with the parameters given in the text.

The agreement between theory and experiment suggests that the behavior of supercritical fluid nitrogen can be described in a manner similar to that of a hard sphere liquid. Therefore, both dispersive attractive and steep repulsive interactions characteristic of the liquid state play an important role in the supercritical phase of nitrogen even at densities smaller than those in the liquid. Consequently, the hard sphere model (WSA theory) and mean spherical approximation used to determine the hard sphere diameter can be employed for the description of the supercritical phase. Nonetheless the results indicate that the temperature effect on the transition energy shifts due to the change of the thermal population of states cannot be entirely neglected. This effect, although small, competes with the transition shift due to temperature induced change of isobaric density and has not been accounted for by the SC theory.

Unfortunately, we are not able to perform analogous high pressure experiments in the liquid phase of nitrogen, due to insufficient equilibrium solubility of benzene in liquid nitrogen. Thus, behavior of the liquid and supercritical phases of nitrogen cannot be directly compared. Nonetheless, comparing the results of calculations and experiment for supercritical nitrogen with those for liquid propane[8] one finds that the behavior in both instances is quantitatively similar; absorption and emission shifts are linear functions of density and are well described by the SC theory. The relative energy shift as a function of normalized density for benzene in propane is larger than for benzene in nitrogen. This effect is presumably due to the larger polarizability of propane (6.48 Å^3) compared to nitrogen (1.76 Å^3); the larger shift is predicted by the SC theory. Further experiments performed in different solute/solvent systems in both liquid and supercritical phases are needed in order to obtain a quantitative estimation of the shift-polarizability relation.

Although the relative energy shifts of benzene as a function of microscopic density in both nitrogen and propane predicted by the SC theory agree reasonably well with the experimental data, the calculated absolute values of the energy shifts between vapor and fluid (liquid) phases at $\rho_0 = 750$ kg m^{-3} are too large: -1510 instead of -272 cm^{-1} for benzene in propane[8] and -1710 instead of -140 cm^{-1} for benzene in supercritical nitrogen. This discrepancy is presumably due to the use of the two parameter harmonic oscillator model and to the neglect of the existence of many other electronic states with different transition oscillator strengths.[5] Fortunately, this discrepancy has a negligible impact on the relative energy shifts calculated by the SC theory.

IV. CONCLUSIONS

Optical absorption spectra of the $^1B_{2u} \leftarrow {}^1A_{1g}$ transition of benzene dissolved in supercritical fluid nitrogen are studied as a function of pressure, temperature, and density. Pressure and density dependences of the $^1B_{2u} \rightarrow {}^1A_{1g}$ emission transition are determined at room temperature. The experimental results for the absorption energy shifts are compared to the theoretical calculations of the Onsager–Böttcher and Wertheim dielectric models, as well as to the microscopic quantum statistical mechanical theory of Schweizer and Chandler.

The main experimental findings are as follows:

(1) Both absorption and emission spectra exhibit similar energy shifts to the red with increasing pressure at constant temperature. Absorption spectral features exhibit small shifts to the red with decreasing temperature at a constant low pressure due to the simultaneous increase of density. The energy shifts are a linear function of density and almost vanish when density is kept constant. This indicates the important microscopic nature of density for the spectroscopic behavior of benzene in supercritical nitrogen. The density dependence of the transition energy shift is slightly less steep at low temperatures thus indicating that the change in the equilibrium thermal population of states also has an impact on the energy shift and cannot be entirely neglected.

(2) Absorption half-widths increase with both pressure and temperature due to either a change in the kinetic energy (population of states) or change of the intermolecular potential caused by the change of density. The temperature dependence of absorption bandwidths has not been observed for benzene in liquid propane most probably because the corresponding density change in the liquid state is much smaller than that in the supercritical fluid phase.

The above results can be interpreted qualitatively by the changes of the intermolecular potential in the ground and excited electronic states described in detail for the benzene/propane system.[8] Both changes in shape and separation of the ground and excited state potentials are considered to be density dependent.

A comparison of the experimental absorption energy shifts with those calculated by the existing theories of solvent effects on solute electronic spectra gives the following results:

(1) Dielectric Onsager–Böttcher and Wertheim models agree roughly with the experimental results of the absorption energy shift as a function of density; however, specific temperature dependent proportionality constants must be employed in the fitting procedure. The energy shifts can be reproduced knowing the density (temperature and pressure) dependence of the dielectric constant and the temperature dependent "fitting" parameter k.

(2) Calculations of the relative energy shifts within the framework of the quantum statistical mechanical theory of Schweizer and Chandler give faithful agreement with the experiment over a large range of densities in supercritical nitrogen. The calculated absolute value of the energy shift, however, is larger than experimentally observed. This can be ascribed to specific simplifying assumptions in the theory.

The liquid state theories appear to be surprisingly accurate for the supercritical phase of nitrogen. Apparently, liquid state theories may be used, at least in some cases, for description of supercritical fluids. In particular, the hard sphere model and mean spherical approximation seem to be valuable liquid state approaches which can be applied to the supercritical phase, at least in the region of liquid-like densities. This notion needs to be confirmed by performing similar studies in different solute/solvent systems, especially those which would admit a simultaneous study and comparison of both liquid and supercritical solution phases.

Comparison of the results with the previous data for benzene in propane[8] confirms qualitatively the theoretical prediction that larger energy shifts occur for solvents characterized by a higher molecular polarizability. This result needs to be verified quantitatively by comparing behavior of different solvents in their liquid phase.

Finally, we note that the OB and W theories are in much better agreement with the supercritical nitrogen fluid data than they are with the liquid propane data. In the latter instance the values of the parameter k are set by the gas to liquid shift value. For the present data fitting, the values of k are not so constrained and only relative energy shifts in a single phase need be of concern.

[1] F. Li, J. Lee, and E. R. Bernstein, J. Phys. Chem. **86**, 3606 (1982).
[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. **87**, 254 (1983).
[4] F. Li, J. Lee, and E. R. Bernstein, J. Phys. Chem. **87**, 1175 (1983).
[5] K. S. Schweizer and D. Chandler, J. Chem. Phys. **78**, 4118 (1983).
[6] E. R. Bernstein and J. Lee, J. Chem. Phys. **74**, 3159 (1981).
[7] M. W. Schauer, J. Lee, and E. R. Bernstein, J. Chem. Phys. **76**, 2773 (1982).
[8] R. Nowak and E. R. Bernstein, J. Chem. Phys. **87**, 3197 (1987).
[9] D. E. Sullivan and J. M. Deutch, J. Chem. Phys. **65**, 5315 (1976).
[10] L. Onsager, J. Am. Chem. Soc. **58**, 1486 (1936); C. J. F. Böttcher, *Theory of Electric Polarization* (Elsevier, Amsterdam, 1973).
[11] M. S. Wertheim, Mol. Phys. **25**, 211 (1973).
[12] J. W. Eastman, J. Chem. Phys. **49**, 4617 (1968).
[13] C. S. Parmenter, Adv. Chem. Phys. **22**, 365 (1972).
[14] W. W. Robertson and S. E. Babb, Jr., J. Chem. Phys. **28**, 953 (1958).
[15] S. E. Babb, Jr., J. M. Robinson, and W. W. Robertson, J. Chem. Phys. **30**, 427 (1959).
[16] W. W. Robertson and A. D. King, Jr., J. Chem. Phys. **31**, 473 (1959).
[17] B. A. Younglove, J. Phys. Chem. Ref. Data **11**, Suppl. 1 (1982).

[18] S. Sambursky, A. Halperin, and H. Henig, J. Chem. Phys. **21**, 2041 (1953).
[19] J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1954).
[20] R. D. Levin and S. G. Lias, Natl. Stand. Ref. Data Ser., Natl. Bur. Stand. 71 (1982).
[21] J. D. Weeks, D. Chandler, and H. C. Andersen, J. Chem. Phys. **54**, 5237 (1971).
[22] L. Verlet and J.-J. Weis, Phys. Rev. A **5**, 939 (1972).
[23] R. Nowak and E. R. Bernstein, J. Chem. Phys. (to be published).