Local density inhomogeneities detected by Raman scattering in supercritical hexafluorobenzene*

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Abstract: The influence of the local density inhomogeneities in supercritical hexafluorobenzene C_6F_6 has been assessed using Raman spectroscopy.

The polarized and depolarized profiles associated with the $\nu_1(A_{1g})$ "breathing" mode of the molecule has been analyzed for the fluid in a wide density range ($0.1 \leq \rho^* = \rho/\rho_C \leq 3$), namely under isothermal conditions ($T^* = T/T_C \sim 1.11$ and close to the critical isotherm $T^* \sim 1.02$).

The evolution upon the density of the band center position of the isotropic profile along the near-critical isotherm showed an anomalous behavior, characterized by a plateau in the density range ($0.6 \leq \rho^* = \rho/\rho_C \leq 1.3$), which is not observed along the isotherm $T^* \sim 1.11$. It has been interpreted as due to the existence of local density inhomogeneities and the density enhancement factor has been evaluated.

The rotational dynamics of the main symmetry axis of the molecule is governed by a diffusional process. The rotational correlation time τ_{2R} exhibits an anomalous behavior (plateau regime) for both isotherms.

These findings put in evidence the existence of local density inhomogeneities in a pure fluid and show that Raman spectroscopy is well adapted to investigate these phenomena.

INTRODUCTION

Spectroscopic and theoretical investigations of local density inhomogeneities (LDIs) in supercritical fluids (SCFs) are a subject of current interest; this subject has been extensively reviewed [1–3]. The main advantage of SCF is the possibility to continuously vary the density from liquid to gas-like values by contouring the critical point. It is in this region, where the highest values of compressibility of the fluid are observed, that the existence of LDIs has been put in evidence. They appear as a consequence of the long-range spatial fluctuations due to the vicinity of the critical point.

Spectroscopic investigations have revealed an enhancement of the local density comparatively with the bulk density (average density of the fluid) along a near-critical isotherm. The main evidence came from the solvatochromic shift observed in UV–visible spectroscopy for electronic transitions in a solute very diluted in an SCF (generally CO_2) along the isotherm $T^* = T/T_c = 1.01$. This peculiar be-

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havior vanished with increasing temperature and was barely detected at $T^* = 1.11$. Along this isotherm, only a monotonous evolution of the shift is observed.

Vibrational spectroscopy is also a powerful tool to get insight into the LDI effects [4,5] through a judicious selection of the normal modes of vibration of the solute molecule. In Raman spectroscopy, the vibrational and rotational relaxation processes of the solute can be separately accessed from band shape analysis. Therefore, it becomes possible to discuss the influence of the density inhomogeneities on the monomolecular dynamics. As far as we know, such investigations have not been reported for a pure fluid.

The present investigation is aimed at providing evidence of the influence of LDI on the evolution of the band center position and the band shape for a pure fluid as a function of the density along a near-critical isotherm ($T^* = 1.02$) in comparison with the evolution along the isotherm $T^* = 1.11$ taken as a reference, for which the LDI is thought to be negligible. In this experimental study, we have chosen the intense totally symmetric vibration A_{1g} ("ring-breathing" mode) of the hexafluorobenzene molecule (C_6F_6) which is a sensitive probe of the intermolecular dynamics.

EXPERIMENTAL

The polarized $I_{VV}(\bar{v})$ and depolarized $I_{VH}(\bar{v})$ profiles have been recorded using the usual 90° scattering geometry and the isotropic $I_{iso}(\bar{v})$ and anisotropic $I_{aniso}(\bar{v})$ profiles have been obtained according to [6]:

$$I_{iso}(\bar{v}) = I_{VV}(\bar{v}) - 4/3\ I_{VH}(\bar{v}) \tag{1}$$

$$I_{aniso}(\bar{v}) = 1/15\ I_{VH}(\bar{v}) \tag{2}$$

The I_{VV} and I_{VH} spectra were recorded in the spectral range 510 to 600 cm^{-1} with a resolution of 0.5 cm^{-1} and a step of 0.1 cm^{-1} on a DILOR Z24 triple monochromator spectrometer with a Spectra Physics krypton-ion laser operating at 647.1 nm. Spectra have been accumulated (6 to 10 for I_{VH}) to improve the signal-to-noise ratio. The band center position has been measured with an accuracy of 0.2 cm^{-1}. The spectrometer has been calibrated by recording the emission line at 671.704 nm of a neon bulb at the different thermodynamics states of the hexafluorobenzene.

The Raman cell made of titanium has four windows; two of them in silica were used for the incident and the scattered light of the laser beam. The other windows were made of sapphire allowing us, respectively, to provide a visual observation of the sample during the experiments and the exit of the light of the laser beam. The critical transition of the hexafluorobenzene was observed and the experimental critical parameters were found to agree, within the experimental uncertainties, with those reported in the literature ($P_C = 3.273$ MPa, $T_C = 516.73$ K, $\rho_C = 555$ kg m^{-3}) [7]. The values of the density of C_6F_6 at the different thermodynamics states were taken from our previous work on the structure of this fluid by neutron diffraction [8]. Raman spectra were recorded in a wide density domain, namely along the isotherms at 528 K and 573 K (respectively, $T^* = 1.02$ and $T^* = 1.11$) with a temperature accuracy of ±1 K, in the pressure range 0.1 to 16 MPa, using the equipment previously described [9].

ANALYSIS AND DISCUSSION

The isotropic $I_{iso}(\bar{v})$ and anisotropic $I_{aniso}(\bar{v})$ profiles of the v_1 totally symmetric "ring-breathing" mode of the molecule for three representative thermodynamics states are displayed in Fig. 1. The band shapes were found to be close to Lorentzian in the density and temperature range investigated.
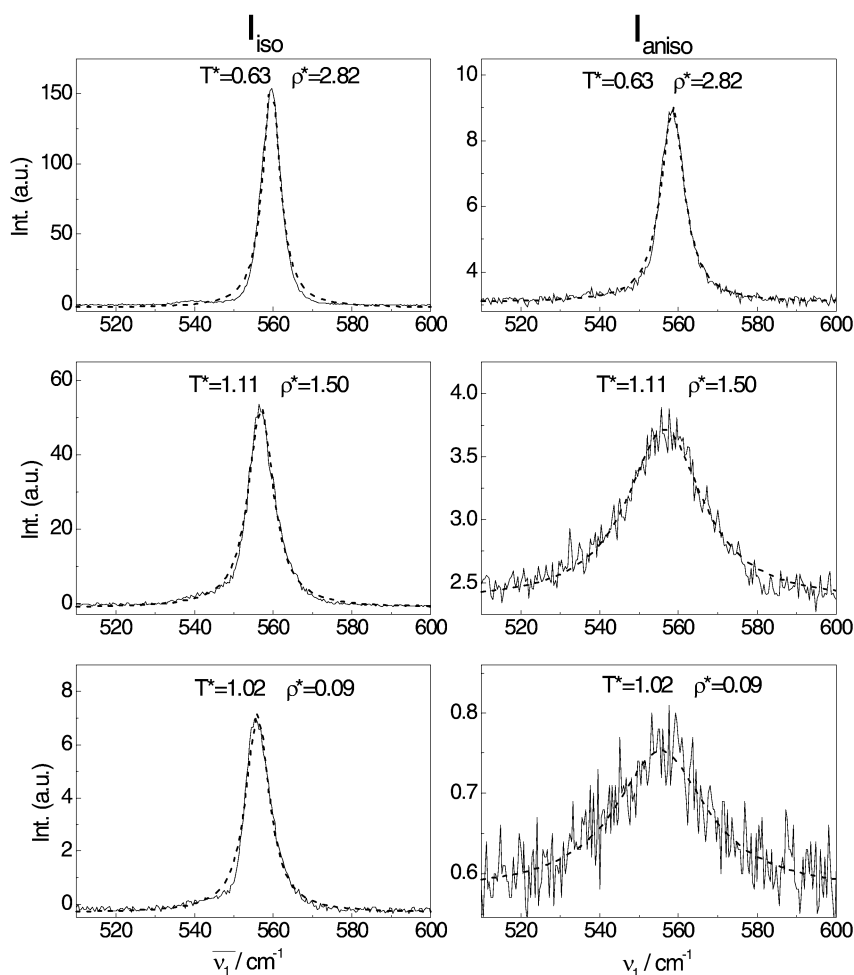
Fig. 1 Isotropic I_{iso} and anisotropic I_{aniso} profiles of the v_1-symmetric "ring-breathing" mode of the hexafluorobenzene (intensities in arbitrary units). The dashed line refers to fitted Lorentzian profile.

Band center position

The evolution of the band center position of the isotropic profile along the isotherm $T^* = 1.11$ and along two isobars ($P^* = 3.36$ and $P^* = 4.89$) as a function of the reduced density $\rho^* = \rho/\rho_C$ is reported in Fig. 2. The band center position increases continuously with the density and can be described by a second-order polynomial (see Fig. 2). We have taken this variation as the expected one for a fluid along a thermodynamics path for which the effect of the neighborhood of the critical point is supposed negligible. In fact, no anomalous behavior appears, and therefore we considered this evolution as representative of the one of a *fluid of reference*. In contrast, along the near-critical isotherm $T^* = 1.02$ a peculiar behavior is observed in the density range, $0.2 < \rho^* < 1.3$. Three well-defined regimes are observed: firstly, at low densities the shift increases to reach a plateau at intermediate density values, and finally, at higher density the shift increases again with values matching those of the reference fluid. A similar trend has been already reported in UV–visible studies and has been interpreted as due to the influence of the LDI in the building of the neighboring shells on going from the isolated molecule (low-pressure gas) toward a molecule completely solvated as in a liquid [1–3].
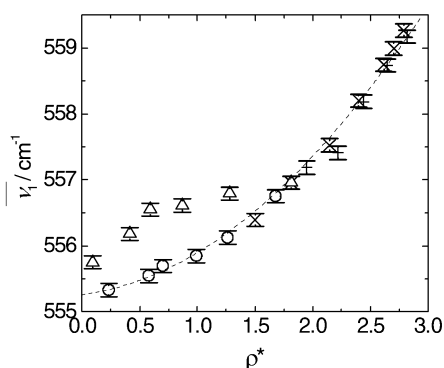
Fig. 2 Evolution of the band center position of the isotropic profile as a function of the reduced density ρ^* along the near-critical isotherm $T^* = 1.02$ ($\triangle$) and along the isotherm $T^* = 1.11$ (O) and for the isobars $P^* = 3.36$ (X) and $P^* = 4.89$ (+). The dashed line is a fitted second-order polynomial.

The local density enhancement can be quantified and extracted from these results. We have used a similar approach as the standard one reported in the literature for solvatochromic shifts in the UV–visible to obtain the values of the local density ρ_{loc}^* [1–3,10]. We have taken the variation observed for the *reference fluid* as the evolution of the band center position with the bulk density ρ^*. This evolution of the local density enhancement $\delta\rho^*$ (in reduced units, defined as $\delta\rho^* = \rho_{loc}^* - \rho^*$) along the near critical isotherm is displayed in Fig. 3.
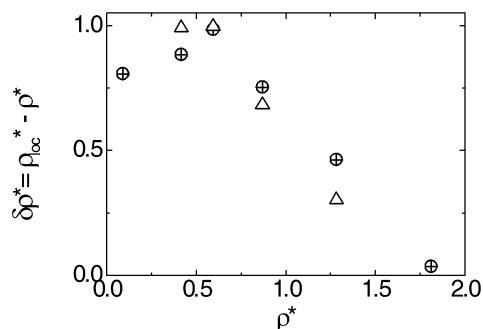

Fig. 3 Reduced local density enhancement $\delta\rho^* = \rho_{loc}^* - \rho^*$ as a function of the density taken from the evolution of: ($\oplus$) the band center position, ($\triangle$) the rotational correlation time (see text).

A nonmonotonous variation, presenting a maximum value for reduced densities close to 0.6 is observed. This trend agrees with that already reported in literature for a solute diluted in an SCF [1–3,10]. It should be pointed out that the strongest variation of the local density in the solvation process occurs mostly at low and intermediate bulk densities $\rho^* < 1.3$. When the bulk density departs markedly from the critical value, the density enhancement strongly decreases and becomes almost vanishing for $\rho^* \sim 2$.

Rotational relaxation

We can obtain information on the LDI effects from the evolution with the density of the rotational correlation time τ_{2R} associated with the rotational relaxation process of the main symmetry axis of the molecule (tumbling motion). This correlation time is equal to $(\pi c \, \Delta v_{rot})^{-1}$ and can be extracted from the full width at half-height (FWHH) (Δv) of the anisotropic and isotropic profiles assuming that vibrational and rotational processes are uncoupled. Because the band shapes are reasonably well de-

scribed by Lorentzian profiles, the contribution of the rotational relaxation to the width of the anisotropic profile is calculated as [6]:

$$\Delta \bar{v}_{rot} = \Delta \bar{v}_{aniso} - \Delta \bar{v}_{iso} \tag{3}$$

The evolution with the density of the rotational correlation time τ_{2R}^*, in reduced units, $[\tau_{2R}^* = \tau_{2R} (kT/I_\perp)^{1/2}, I_\perp$ is the momentum of inertia about the main symmetry axis of the molecule] is displayed in Fig. 4. As the fast modulation criterion $\tau_{2R}^* > 1/\sqrt{6}$ is always fulfilled and band shapes are close to Lorentzian profiles, we may conclude that the molecular reorientation of the main symmetry axis of the molecule is governed by a diffusional process.
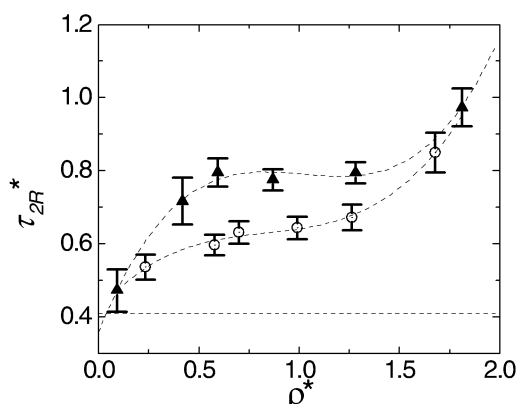

Fig. 4 Evolution of the rotational correlation time τ_{2R}^* as a function of the density for the isotherms $T^* = 1.11$ (○) and $T^* = 1.02$ (▲). The horizontal dashed line refers to the fast modulation criterion [6].

Along the isotherm $T^* = 1.11$ the evolution of τ_{2R}^* with the density is highly nonlinear and presents a plateau regime in the density range $0.5 < \rho^* < 1.3$ (Fig. 4).

This variation put in evidence a gradual rotational hindering with increasing density values. An estimation of the mean angular rotational step $<\theta> = (6\tau_{2R}^*)^{-1}$ leads to values decreasing from about 15°, for the density range $0.6 < \rho^* < 1.0$, to about 2° at liquid densities, for which the rotational diffusion limit applies. Along the isotherm $T^* = 1.02$, the same trend is observed but the values of τ_{2R}^* are higher due to a slower rotational dynamics at lower temperature. Taking as reference the variation of τ_{2R}^* with ρ^* for $T^* = 1.11$, we have calculated from this evolution, the reduced local density enhancement $\delta\rho^*$, the values of which are displayed on Fig. 3. These values are compared on this figure with those obtained from the study of the band center position. Clearly, the same trend is observed, and we note a good agreement between the values of the reduced local density enhancement $\delta\rho^*$ obtained from band center position and rotational correlation time. This result proves that the LDI is also reflected into the rotational dynamics process. Therefore, we may infer that the rotational dynamics is also a good probe and provides another way to study this phenomenon.

CONCLUSION

This study shows that the LDI effects can be detected not only for a solute diluted in an SCF as reported in the literature, but also for neat fluid. We also emphasize that Raman scattering is a valuable and promising technique to get insight on the LDI from both static (band center position) and dynamics (rotational relaxation) information. At last, we would like to stress that the approach used to extract an en-

hancement factor characterizing LDI deserve to be more firmly grounded from the theoretical point of view.

ACKNOWLEDGMENTS

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