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Vibrational and rotational relaxation of hexafluorobenzene studied by Raman scattering in the supercritical domain

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This paper is dedicated to Professor Jack Yarwood for his retirement

Abstract

The vibrational and rotational relaxation of hexafluorobenzene (C_6F_6) has been studied by Raman spectroscopy in the supercritical domain. The polarized $I_{VV}(\nu)$ and depolarized $I_{HV}(\nu)$ profiles associated with the vibrational $\nu_1(A_{1g})$ 'breathing' mode of the molecule have been analysed for the fluid under isothermal ($T^* = T/T_C \sim 1.23$ and 1.02) and isobaric conditions ($P^* = P/P_C \sim 3.34$ and $P^* \sim 4.89$) in a wide density domain ($0.02 \leq \rho^* = \rho/\rho_C \leq 3$). The band shapes were found to be close to Lorentzian profiles in the density and temperature range investigated.

The band centre position shifts towards higher frequency values with density. These shifts have been discussed in terms of the competition between repulsive and attractive forces using the Buckingham-Ben-Amotz approach. It was found that repulsive interactions are dominant and that the attractive interactions are mostly effective at low densities. As for the vibrational relaxation, the analysis has been done in the framework of the dephasing mechanism. In the domain of liquid-like densities the experimental vibrational times follow the Isolated Binary Collision (IBC) model (Fischer-Laubereau), derived for a repulsive interaction. In contrast, along the isotherms in the gas-like density values, such a model does not apply. As a consequence, it appears that attractive interactions play a significant role, in the gas-like density domain. As the rotational dynamics of the main molecular axis (tumbling motion) obeys the fast modulation condition, the molecular reorientation process is governed by a diffusional process.

Along the near critical isotherm and in the high compressible domain, local density inhomogeneities are found to have strong influence on both measured shifts and rotational correlation times. A local density excess $\delta\rho^* = \rho^*_{\mathrm{loc}} - \rho^*$ has been featured from these two observables. Furthermore, a very large activation volume was found (800 cm^3 mol^{-1}) which is due to the clustering phenomenon taking place in the hyper-compressible domain.

Keywords: Vibrational and rotational relaxation; Supercritical; Hexafluorobenzene; Raman spectroscopy

1. Introduction

The study of vibrational and rotational relaxation from the analysis of the isotropic and anisotropic Raman bands is a subject of considerable interest in liquid phase [1,2]. The use of supercritical fluids (SCF) offers an unique opportunity to revisit the balance between the repulsive and attractive forces as the density can be continuously varied from liquid to gas like values by contouring the critical point. Moreover, the high values of compressibility of SCF in the vicinity of the critical point lead to the local density inhomogeneities which have been extensively reviewed by spectroscopic and theoretical investigations [3–7].

Such inhomogeneities lead to local density enhancement due to the long range spatial density fluctuations. The main evidences came out from the solvatochromic shift observed in UV–Visible spectroscopy for electronic transition of a solute very diluted in a SCF (generally CO_2), along the near critical isotherm $T^* = T/T_C = 1.01$.

Vibrational spectroscopy can be a powerful tool to detect local density inhomogeneities effects through a judicious selection of the normal modes of vibration of the solute

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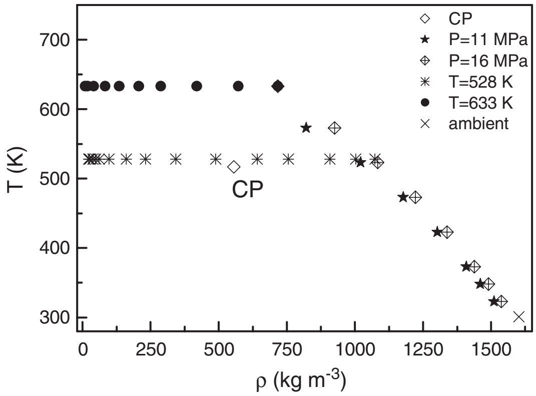

Fig. 1. Experimental thermodynamics points along: isobars 11MPa and 16MPa; isotherms 528 K and 633 K. Critical point (CP) is reported too.

molecule [8,9]. In Raman spectroscopy, the vibrational and rotational relaxation processes of the solute can be separately accessed from a band shape analysis. As far as we know, such investigations have only been scarcely reported for a pure fluid [10–15]. A special reference should be done to the detailed work performed on the Raman line broadening near the critical point for pure fluids and isotopic mixtures [16–19].

The present study is aimed at providing insights on the competition between repulsive and attractive forces and to characterize the local density enhancement phenomenon from the evolution of both band centre position and bandshape as a function of the density. For this purpose, we have carried out this investigation from the intense A_{1g} totally symmetric ring breathing mode of hexafluorobenzene (C_6F_6).

2. Experimental

The polarized $I_{VV}(v)$ and depolarized $I_{HV}(v)$ Raman spectra were recorded on a Jobin-Yvon HR800 spectrometer with a Spectra Physics krypton-ion laser source operating at a wavelength of 752.5 nm with a power of 150 mW. Spectra were recorded using the back-scattering geometry in the spectral range 450–650 cm^{-1} with a resolution of 0.6 cm^{-1} using a 1800 lines mm^{-1} grating. To improve the signal to noise ratio several $I_{VV}(v)$ and $I_{HV}(v)$ spectra have been accumulated for typical times of 5 and 20 min, respectively. In order to take accurate line positions the spectrometer has been calibrated by recording the 783.9 nm emission line of a neon bulb. We have used the pressure bench and the Raman cell equipped with fused silica and sapphire windows previously described [20]. Using this setup, we were able to observe the critical transition of the hexafluorobenzene and to check the critical parameters reported in the literature [21]. Our measurements agree well with the values $P_C=3.327$ MPa and $T_C=516.73$ K which correspond to the critical density $\rho_C=555$ kg m^{-3}. The values of the density of C_6F_6 at the different thermodynamic points were taken from our previous work [22] on the structure of this fluid by neutron diffraction. Raman spectra were recorded at ambient conditions, along the isobars 11 MPa and 16 MPa ($P^*=3.36$ and $P^*=4.89$, respectively) and the isotherms 528 K and 633 K ($T^*=1.02$ and $T^*=1.23$, respectively). The experimental thermodynamic points are displayed on Fig. 1.

3. Analysis and discussion

The isotropic $I_{iso}(v)$ and anisotropic $I_{aniso}(v)$ profiles have been obtained from the polarized $I_{VV}(v)$ and depolarized $I_{HV}(v)$ Raman profiles according to [2]:

$$I_{iso}(v) = I_{VV}(v) - 4/3\ I_{HV}(v) \qquad (1)$$

$$I_{aniso}(v) = 1/15\ I_{HV}(v). \qquad (2)$$

The isotropic and anisotropic profiles associated with the v_1 vibration of hexafluorobenzene molecule at two representative thermodynamic states are displayed on Fig. 2. The band shapes were found to be close to Lorentzian in the density and temperature range investigated.

3.1. Vibrational relaxation

3.1.1. Frequency shift

The evolution with the reduced density $\rho^*=\rho/\rho_C$ of the band centre position along the isotherms and isobars is displayed on Fig. 3a. Clearly, the band centre positions of the isotropic profile at $T^*=1.23$ monotonously increase with the density and reach values merging with those measured along the two isobars ($P^*=3.34$ and $P^*=4.89$) at density close to 1.7. Because along this thermodynamic path, the effects due to the neighbourhood of the critical point are supposed negligible (as $T^*>1.1$), we have considered this evolution as representative as that of a *fluid of reference*. In contrast, we observe an anomalous evolution for densities $\rho^*<1.5$ along the near critical isotherm. At low densities, the shift of the band centre position increases to reach a plateau at intermediate density ($0.7\leq\rho^*=\rho/\rho_C\leq1.7$). It increases again at higher density to reach the values corresponding to that of the reference fluid. It is noteworthy that a similar trend was previously reported in UV–Visible studies for a solute dissolved in a SCF fluid and has been interpreted as a local

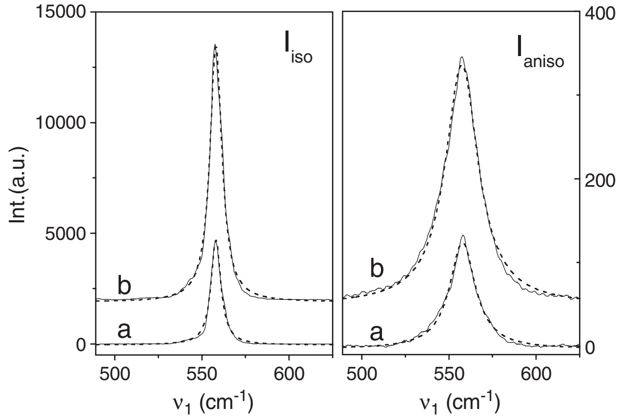

Fig. 2. Isotropic and anisotropic profiles associated with the totally symmetric A_{1g} (ring breathing) v_1 mode in the fluid C_6F_6 at: (a) $T=528$K, $P=3.7$MPa, $\rho^*=0.42$; (b) $T=633$ K, $P=16$ MPa, $\rho^*=1.29$ (reduced density $\rho^*=\rho/\rho_C$).