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The dense phase of CO_2-CS_2 mixtures has been analysed by Raman spectroscopy as a function of the CO_2 concentration (0.02–0.95 mole fractions) by varying the pressure (0.5 MPa up to 7.7 MPa) at constant temperature (313 K). The polarised and depolarised spectra of the induced (ν_2, ν_3) modes of CS_2 and of the ν_1-$2\nu_2$ Fermi resonance dyad of both CO_2 and CS_2 have been measured. Upon dilution with CO_2, the evolution of the spectroscopic observables of all these modes displays a "plateau-like" region in the CO_2 mole fraction 0.3–0.7 never previously observed in CO_2-organic liquids mixtures. The bandshape and intensity of the induced modes of CS_2 are similar to those of pure CS_2 up to equimolar concentration, after which variations occur. The preservation of the local ordering from pure CS_2 to equimolar concentration together with the non-linear evolution of the spectroscopic observables allows inferring that two solvation regimes exist with a transition occurring in the plateau domain. In the first regime, corresponding to CS_2 concentrated mixtures, the liquid phase is segregated with dominant CS_2 clusters, whereas, in the second one, CO_2 monomers and dimers and CO_2-CS_2 hetero-dimers coexist dynamically on a picosecond time-scale. It is demonstrated that the subtle interplay between attractive and repulsive interactions which provides a molecular interpretation of the non-ideality of the CO_2-CS_2 mixture allows rationalizing the volume expansion and the existence of the plateau-like region observed in the pressure-composition diagram previously ascribed to the proximity of an upper critical solution temperature at lower temperatures. © *2013 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4821593]

I. INTRODUCTION

Vibrational spectroscopic studies of carbon dioxide and carbon disulfide have always attracted a great interest as being simple highly symmetric linear tri-atomic molecules. In gaseous phase, investigations have been mainly devoted to the analysis of the Fermi resonance coupling of vibrational modes of the isolated molecule,[1–3] and to the characterisation of the structure of weakly bounded clusters.[4–17] In dense phase, the aim was to provide insight on the nature and time scale of the intermolecular interactions from "allowed" vibrational spectra or from the analysis of collision induced (CI) spectra which are unique probes of the multi-body interactions.[18–36]

The study of the interaction of carbon dioxide with molecular liquids and complex fluids as ionic liquids is a field of current interest,[37–66] motivated not only from the fundamental point of view but mainly under the impetuous motivation of understanding the interactions of CO_2 in the field of environmental studies.[67–70] Surprisingly, in this context, studies of the CO_2-CS_2 binary mixture are extremely scarce. In gaseous phase, a single spectroscopic study using infrared laser to probe the asymmetric stretch of CO_2 in a CO_2-CS_2

(1:2) mixture in helium has been performed and the formation of a weak complex with a non-planar X-shaped structure (C_{2v} symmetry) has been put in evidence.[71] In dense phase, investigations have been limited to thermodynamic measurements of the phase diagram equilibrium of this system and found that this mixture belongs to the type II phase diagrams in the classification of Scott and Van Konynenburg.[72,73] It was shown that a successful description of the highly non-ideal behaviour of this phase diagram can be obtained using equations of state which are able to predict the liquid-liquid immiscibility observed on this system.[72,73]

In a series of investigations, we have shown that relevant information on the formation of transient hetero-dimers can be obtained using Raman spectroscopy combined with *initio* calculations to analyse the dense phase of binary mixtures obtained by introducing under pressure supercritical carbon dioxide in organic liquids at constant temperature.[55,58,62,63] In this context, the CO_2-CS_2 mixture appears as an interesting system as the molecules are iso-electronic and have similar shape, but differ in their polarisability and quadrupole moment. The characterisation at the molecular level of the non-ideal behaviour of this mixture and the significance of the plateau like region observed in the pressure-composition diagram at 313 K (Fig. 1), related to the presence of a liquid-liquid equilibrium (LLE) region with an Upper Critical

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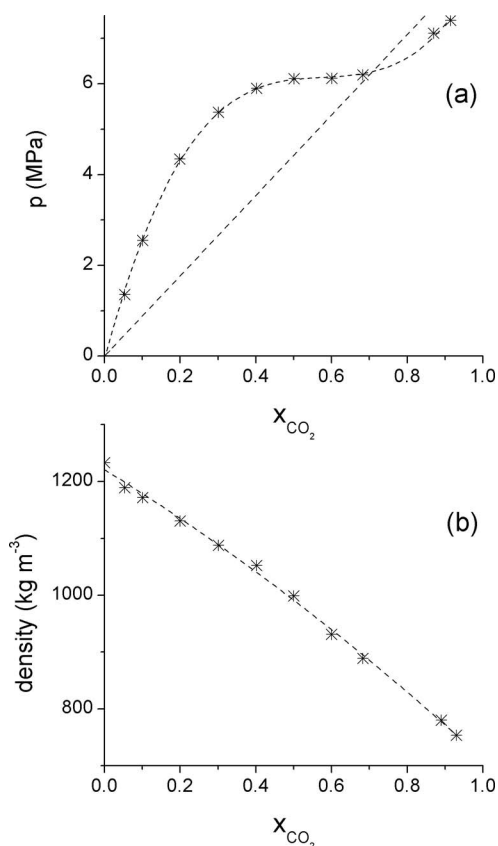
FIG. 1. Pressure-composition diagram of the binary mixtures CO_2-CS_2 (∗) at 313 K (a). The straight line represents the ideal behaviour predicted by Raoult's law. The curve is a fitted third order polynomial. Evolution of the density of the binary mixtures CO_2-CS_2 (b). The curve is a fitted second order polynomial. Data are taken from Carvalho *et al.*[73]

Solution Temperature (UCST) at 290 K,[72,73] are therefore issues which need to be assessed from vibrational spectroscopy.

The paper will be organised as follows. First, we will present the experimental observations using Raman spectroscopy on the ν_1-$2\nu_2$ CO_2 Fermi dyad domain, followed by those on the induced (ν_2 and ν_3) and allowed (ν_1 and $2\nu_2$) modes of CS_2. Then, we will rationalize these observations using the collision induced framework of Madden *et al.* for the forbidden CS_2 modes,[18,20,21,23–32,35] and vibrational relaxation models to discuss the departures from ideality probed by the allowed CO_2 and CS_2 modes. Finally, we will discuss the non ideality of the mixture from the existence of two distinct solvation regimes with a transition characterised by a plateau domain found in the evolution of the spectroscopic observables with the concentration.

II. EXPERIMENTAL

A. Experimental conditions

The polarised I_{VV} and depolarised I_{HV} Raman spectra were recorded on a LabRam HR8000 spectrometer using a back-scattering geometry. The spectral domains of the CO_2 Fermi dyad and of the ν_1 and $2\nu_2$ modes of CS_2 were measured using a Spectra Physics Kr^+ laser operating at 752.5 nm and with a 1800 lines/mm grating giving 0.5 cm^{-1}

spectral resolution. Further measurements in the spectral domains of ν_2 and ν_3 of CS_2 and in the spectral domain between the CO_2 Fermi dyad have been performed at 3.8 cm^{-1} resolution using an Ar^+ laser operating at 514 nm with a 600 lines/mm grating. The spectra have been corrected of the background and the width from the finite effect of the spectral resolution according to the Tanabe's correcting method.[74] Several spectra have been accumulated (at least ten) for typical times of 16 min and 4 min, respectively, for the two sets of measurements. Wavenumber calibration has been performed by recording different emission lines of a neon bulb. We have used the pressure bench and the Raman cell equipped with fused silica windows previously described[75] to work in the 0.1–8.0 MPa pressure range at T = 313 K. Typical raw spectra obtained in the spectral domain of the CO_2 Fermi dyad are displayed in the supplementary material[117] (Fig. SI1). The cell windows give a faint polarised feature at about 470 cm^{-1}, which is not affected, at constant temperature, by the pressure variation (up to 8 MPa) and has been used as an internal standard for intensity calibration of the bending mode of CS_2 (Fig. SI2 of the supplementary material[117]). For the measurements in the mixtures, we initially filled the cell with CS_2 (Aldrich, 99% purity) in order to ensure that, after addition of CO_2 (Air Liquide, purity 99.995%) and pressurization, the incident laser beam always impinges on the liquid phase. The mixtures were continuously stirred using a magnet activated by a rotating magnetic field. All the spectra have been recorded after an equilibrium time greater than 1 h. The pressure-composition diagram and the evolution of the density with the concentration of the CS_2-CO_2 system have been reported for pressures up to 7.39 MPa at 313 K and are displayed in Fig. 1.[73]

B. Experimental observations

The CO_2 and CS_2 molecules have the same $D_{\infty h}$ molecular symmetry and therefore the same vibrational modes, namely, the symmetric ν_1 (Σ^+_g) and asymmetric ν_3 (Σ^+_u) stretch vibrations, and the ν_2 (Π_u) bending mode. The Raman activity of the ν_2 and ν_3 modes is normally forbidden by the selection rules of the isolated molecule. In dense phase, these modes become weakly active, the intensity of ν_3 being always smaller.

1. Carbon dioxide

a. The $2\nu_2$-ν_1 Fermi dyad. The study of the different vibrational modes of CO_2 has been restricted to the $2\nu_2$-ν_1 Fermi dyad, as the ν_2 and ν_3 bands are very weak and also because ν_2 is completely darkened due to its overlap with the intense ν_1 peak of CS_2. The polarised Raman spectra of the CO_2 Fermi dyad measured in the binary mixtures and having their intensities normalised to the total integrated intensity of each component of the dyad are displayed in Fig. 2 and compared with that of pure CO_2 (recorded at a density close to that of the more concentrated mixture). We observe that the band centre position of the Fermi doublet is shifted towards lower frequency values and that their width increases
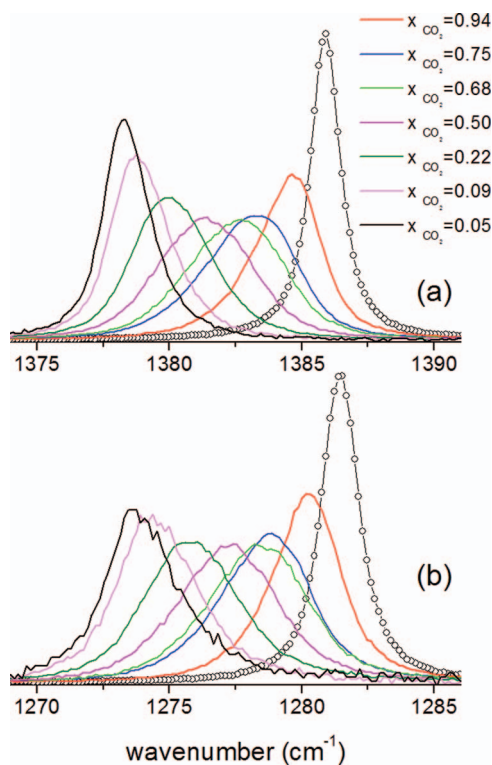
FIG. 2. Raman spectra of the Fermi dyad of CO_2 diluted in CS_2 at increasing CO_2 concentration at 313 K. The intensities have been normalised to the total integrated intensity of each component of the dyad, upper (a) and lower (b). The value of the density of pure CO_2 ($\rho = 743.04$ kg m^{-3}, 13 MPa) was chosen to be close to the more concentrated mixture (x_{CO_2} = 0.94, $\rho = 740$ kg m^{-3}).
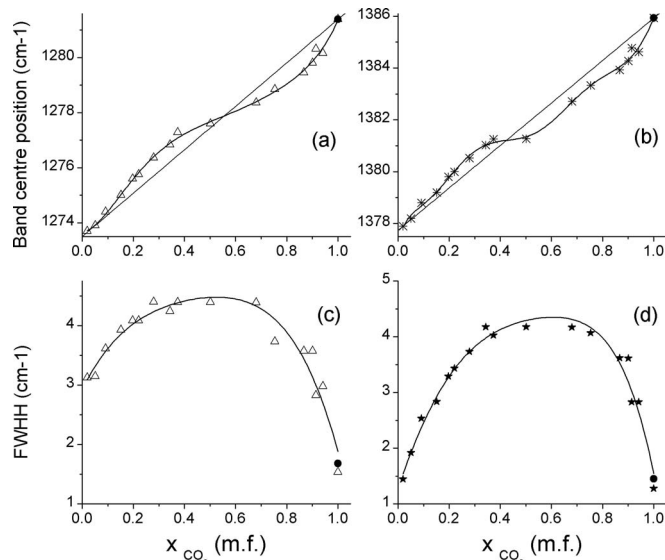

FIG. 3. Evolution with the CO_2 concentration of the band centre position [(a) and (b)] and of the FWHH [(c) and (d)] of the polarised Raman spectra in the CO_2 Fermi dyad domain, lower [(a) and (c)] and upper dyad components [(b) and (d)], of the mixtures at 313 K (from x_{CO_2} 0.02 up to 0.94). The values for pure CO_2 ($\rho = 743.04$ kg m^{-3}, 13 MPa) are also displayed (●). The lines obtained by fitting a third order polynomial and the straight lines are drawn to guide the eyes.

markedly compared to those of pure CO_2. In this spectral range, the spectrum of pure CS_2 is flat.

It is noteworthy that a small amount of CS_2 added to CO_2 ($x_{CO_2} = 0.94$) leads to marked spectral perturbation. Furthermore, the components of the dyad broaden and become asymmetric, as the CO_2 concentration decreases from pure to equimolar concentration, and then narrowed and presented a reverse asymmetry for more concentrated solutions in CS_2.

The evolution of the band centre position and full width of the dyad components is displayed in Fig. 3. A non-monotonous increase of the band-centre with the concentration is observed presenting a plateau-like region in the concentration range 0.3–0.7 mole fraction (m.f.). The width of the dyad components (Fig. 3) increases with the CO_2 concentration, reaches an ill-defined maximum at about 0.5 m.f. and then decreases. The values of the width are about the same at low ($x_{CO_2} \leq 0.2$) and high ($x_{CO_2} \geq 0.8$) CO_2 concentrations. The trends observed for the band centre positions and widths are at variance with the linear behaviour previously observed for CO_2 in binary mixtures.[55,58,62,63]

The ratio R of the integrated intensity of the upper versus lower component of the dyad as a function of the CO_2 concentration is reported in Fig. 4. It decreases with the CO_2 concentration from the limiting values close to those previously measured for CO_2 very diluted in "interacting" solvents[55,58,62,63] to the value observed in neat CO_2 at the same corresponding density. However, in contrast to CO_2 in "interacting" solvents, the present trend is non-linear and presents a

plateau-like region in the concentration domain (0.3–0.7 m.f.) as observed for band centre positions and widths.

b. The spectral domain between the CO_2 dyad peaks. At high CO_2 concentration ($x_{CO_2} \sim 0.9$), a very weak, polarised, broad feature centred at about 1335 cm^{-1} and absent in pure CS_2 is observed (Fig. 5). The shape and band centre position are close to those observed in pure CO_2 and due to the presence of a transient homo-dimer CO_2-CO_2.[10–12,76,77] Upon an increase of the CS_2 concentration in the mixture ($x_{CO_2} \sim 0.7$), a feature with a more symmetric band-shape is
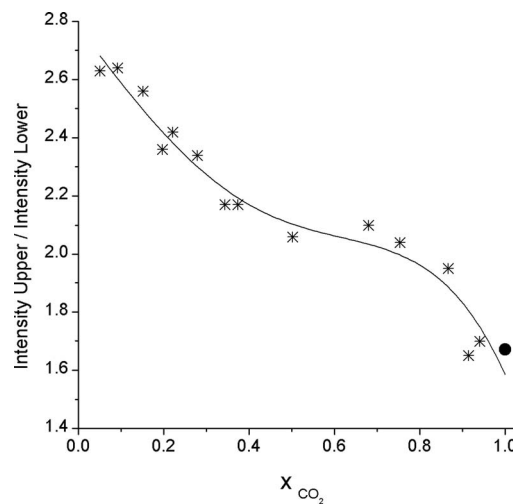

FIG. 4. Evolution with the CO_2 concentration of the ratio R of the integrated intensity of the upper versus lower component of the Fermi dyad. This ratio value for pure CO_2 ($\rho = 743.04$ kg m^{-3}, 13 MPa) is also displayed (●). The line obtained by fitting a third order polynomial is drawn to guide the eyes.
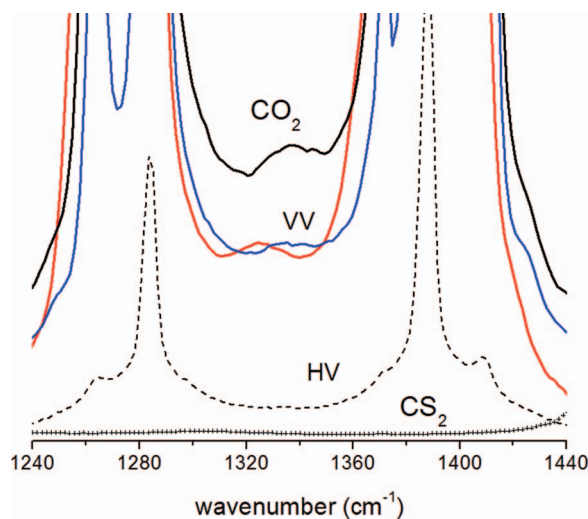
FIG. 5. Polarised Raman profiles in the spectral domain between the CO_2 Fermi dyad peaks in the CO_2-CS_2 mixture at 313 K at two concentrations (blue $x_{CO_2} = 0.91$, red $x_{CO_2} = 0.72$). The polarised spectra of pure CO_2 (13 MPa, black) and of pure CS_2 (+) and the depolarised spectrum of the mixture at $x_{CO_2} = 0.91$ (dashed curve) are given for comparison.

FIG. 6. Polarised (a) and depolarised (b) profiles of the ν_2 and ν_3 induced modes of CS_2 in the pure liquid (black) and in the equimolar mixture (red) at 313 K. The bands observed at about 660 cm^{-1} and 800 cm^{-1} are the ν_1 and $2\nu_2$ of CS_2 and the bands at 1280 cm^{-1} and 1380 cm^{-1} are the components of the CO_2 Fermi dyad.

detected at lower wave-numbers (about 1325 cm^{-1}). The formation of transient hetero dimers between CO_2 and organic liquids has been firmly established from Raman spectroscopic studies combined with *ab initio* calculations on the degeneracy removal of the CO_2 bending mode.[58,62,63,78] This spectral feature has been interpreted as a further evidence of the formation of the hetero-dimer based upon correlation method of group theory.[58,62,63] Therefore, we infer that the feature observed between the Fermi dyad is the signature of the transient CO_2-CS_2 hetero-dimer.

2. Carbon disulfide

a. The ν_2 and ν_3 induced modes. The polarised I_{VV} and depolarised I_{HV} Raman spectra of the ν_2 and ν_3 induced modes of carbon disulfide in the pure liquid and in the equimolar mixture are easily detected (about 395 cm^{-1} and 1520 cm^{-1}, respectively), and do not significantly overlap with other modes (Fig. 6). The band-shapes and band-centre positions of the two modes are almost unaffected by the dilution with CO_2. The values of the depolarisation ratio of the two modes in the pure liquid, within experimental uncertainties, are about the same ($\rho = 0.40 \pm 0.06$) as reported before[18] and found here almost independent of the CS_2 concentration in the mixture. In the pure fluid, the band-shapes of the polarised spectra of the ν_2 and ν_3 modes recorded in the same experimental run are within experimental uncertainties, superposable to their respective depolarised spectra in agreement with previous observation[18] (Figs. 7(a) and 7(b)).

This band-shape similarity is the signature of the collision-induced origin of the spectra.[18,24] Upon dilution, even reaching equimolar concentration, this similarity is preserved for the two modes (Figs. 7(c) and 7(d)). From these results (Figs. 6 and 7), we can conclude that the two induced modes of CS_2 are not affected by the dilution from the neat liquid to equimolar concentration. For more diluted mixtures,
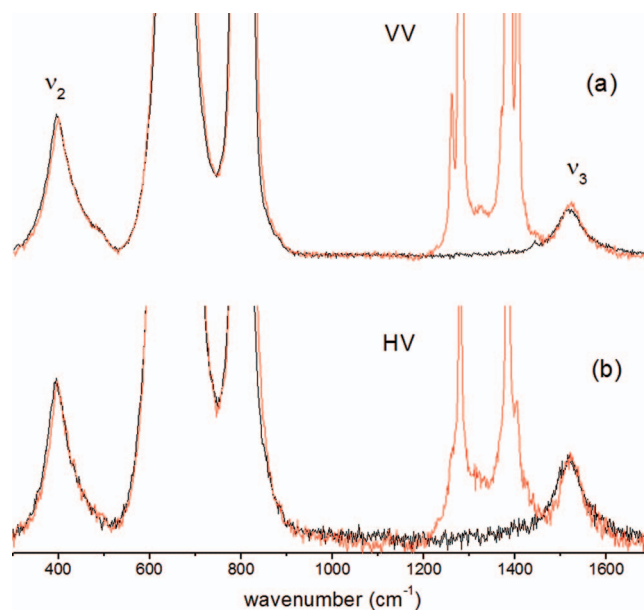
the weak ν_3 mode (three times less intense than ν_2) becomes obscured due to the overlap with the upper component of the CO_2 Fermi dyad precluding this type of comparison. Therefore, we will concentrate on the evolution of the ν_2 mode.

The polarised profiles of the ν_2 mode measured at increasing mole fraction of carbon dioxide and scaled as described in Sec. II A are presented in Fig. 8. The band-shapes are slightly asymmetric having the intensity of their high-frequency side slightly greater than the low-frequency one as reported for the pure liquid.[19,31,35] This specific point is addressed in the supplementary material.[117] The comparison of the profiles shows that upon an increase of the pressure up to
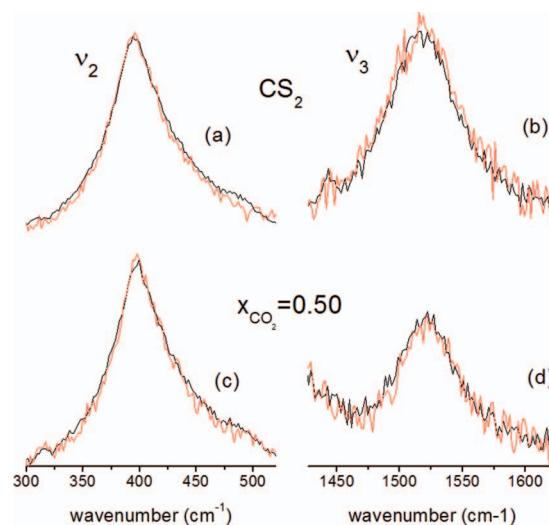

FIG. 7. Comparison of the polarised (black) and depolarised (red) profiles of the ν_2 [(a)and (c)] and ν_3 [(b) and (d)] induced modes of CS_2 in the pure liquid [(a) and (b)] and in the equimolar mixture [(c) and (d)] at 313 K.
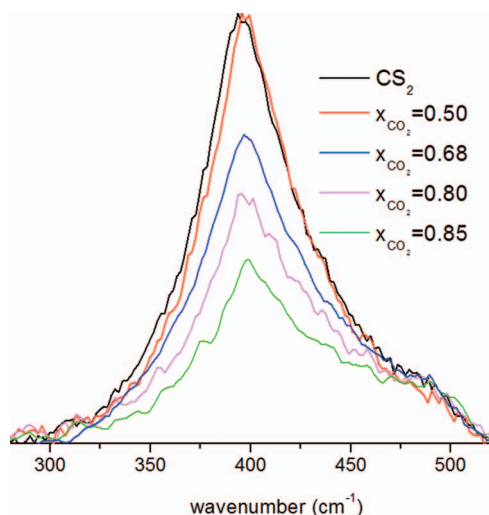
FIG. 8. Evolution of the polarised profiles of the ν_2 mode of CS_2 with the CO_2 concentration at 313 K. The spectra have been scaled as described in the text.

6.1 MPa ($x_{CO_2} = 0.5$), there is no significant variation of the integrated intensity (Fig. 8). By contrast, the intensity of the profiles decreases markedly beyond this state point. Upon a modest increase of pressure (0.1 MPa) above 6.1 MPa, the intensity falls markedly. This trend is consistent with the strong variation of the concentration ranging between $x_{CO_2} = 0.5$ and $x_{CO_2} = 0.68$ (Fig. 1).

The evolution with the CO_2 concentration of the integrated intensity of these profiles normalised to that of pure CS_2 is reported in Fig. 9. As qualitatively seen on the spectra (Fig. 8), the intensity is almost not affected by the CO_2 dilution up to equimolar concentration and then strongly decreases reaching a minimum value at the highest concentration investigated.

This trend is not modified by using volume fraction instead of mole fraction, as they are proportional.[79–81] The intensity evolution can be nicely fitted using a third order polynomial and clearly departs from a straight line drawn to guide the eyes between the two extreme concentrations,
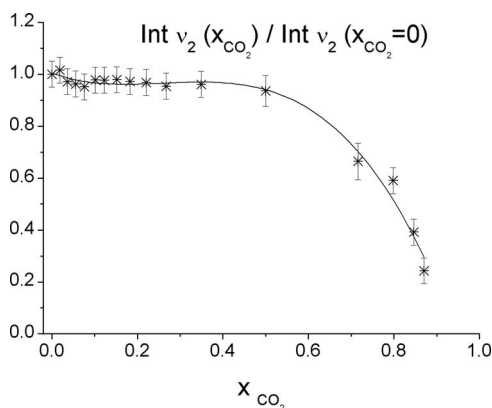

FIG. 9. Evolution with the CO_2 concentration of the integrated intensity of the polarised profiles of the ν_2 mode normalised to that of pure CS_2. The line obtained by fitting a third order polynomial and the straight line between the two extreme concentration are drawn to guide the eyes.

namely, pure CS_2 and CS_2 infinitely diluted in CO_2 for which the intensity is expected to almost vanish. As the spectra of the ν_2 and ν_3 modes have been always measured under the same conditions and because the band shapes of the two induced modes are not affected by the dilution ($x_{CO_2} \leq 0.5$), the ratio of their integrated intensity is the same as in pure CS_2. Therefore, the evolution of the integrated intensity of the two induced modes is almost constant with the CO_2 concentration from the pure CS_2 to equimolar dilution (Fig. 9).

b. The ν_1-$2\nu_2$ Fermi resonance. The ν_1 symmetric stretch vibration, as an allowed Raman mode, gives rise to a strongly active polarised band.[20, 32, 82] In contrast to CI bands, this mode will mainly give access to mono-molecular information (discarding an extremely weak CI contribution acting in its far-wing), and for this reason, will not *a priori* constitute a so-sensitive probe of the intermolecular multi-body interactions as the ν_2 and ν_3 modes. The $2\nu_2$ overtone, which is in principle expected to have a vanishing intensity, is in fact strongly active due to a Fermi resonance coupling with the ν_1 mode. This phenomenon is well known for tri-atomic linear molecules, the best (historical) example being CO_2.[2, 22, 83]

The experimental and theoretical study of the Raman spectra associated with the $2\nu_2$- ν_1 Fermi resonance for CS_2 in the gas phase (and for CO_2 as well) has been explored in elegant studies by Montero *et al.*[2, 3] In liquid CS_2 under high pressure, the influence of inter-molecular interactions on the parameters characterising the Fermi resonance has been discussed by Ikawa *et al.*[31] We note that the strength of the coupling between the ν_1 and $2\nu_2$ modes is much greater in carbon dioxide than in CS_2 due to a greater mixing of the wave functions of the unperturbed states corresponding to these modes.[2, 31] As a consequence, the activity of the $2\nu_2$ mode which borrows its intensity from the ν_1 mode is less effective in CS_2 than in CO_2. This can be clearly seen from the comparison of Figs. 10 and 2. In CS_2, the $2\nu_2$
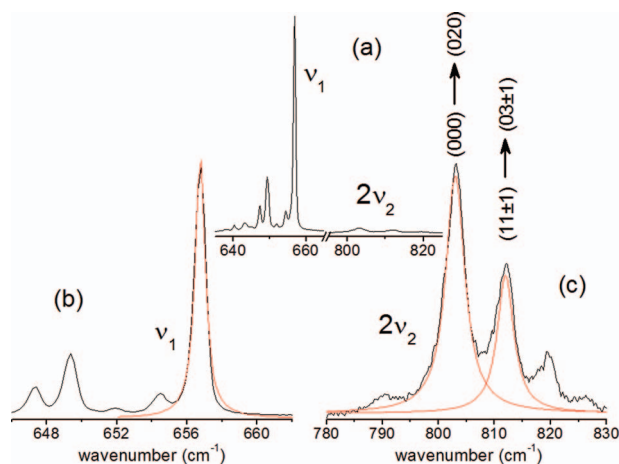

FIG. 10. Polarised spectra of the ν_1 and $2\nu_2$ modes of CS_2 measured at high CO_2 concentration at 313 K (a) ($x_{CO_2} = 0.94$). The fit of the profiles by independent Lorentzian components is reported [(b) and (c)]. The assignment of the transition in the $2\nu_2$ spectral domain (c) is taken from Montero *et al.*[2, 3] according to their labelling of the levels.
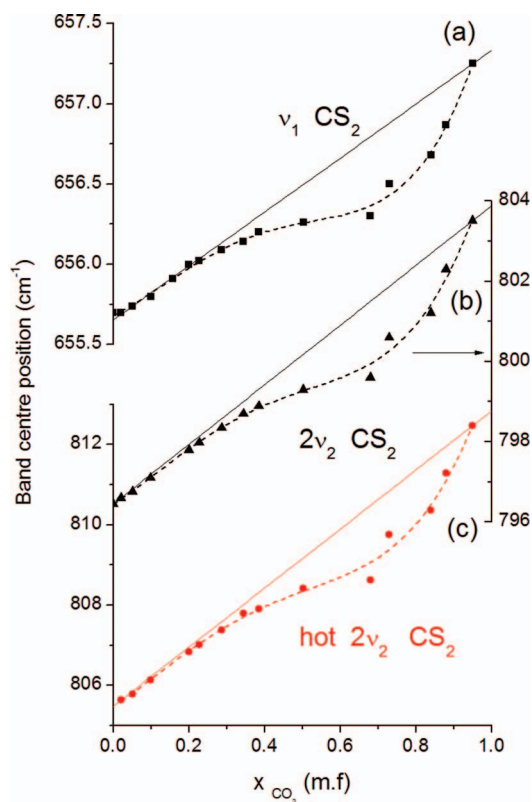
FIG. 11. Evolution of the band-centre positions of the ν_1 (a), $2\nu_2$ (b), and its hot-band (c) of CS_2 with the CO_2 concentration at 313 K. The dashed lines obtained by fitting a third order polynomial are given to guide the eye. The lines obtained by fitting a third order polynomial and the straight lines are drawn to guide the eyes.

The evolution of the band centre positions and FWHH of the ν_1, $2\nu_2$, and its hot-band obtained from the fit of single Lorentzian profiles are reported as a function of the CO_2 concentration in the mixture in Figs. 11 and 12.

It is readily apparent that all the band centre positions increase with the CO_2 concentration in a markedly non-monotonous way, displaying a plateau-like region in the 0.3–0.7 mole fraction range. The width of the ν_1 mode remains almost unaffected by the dilution up to about 0.7 m.f. and decreases at higher concentration. The widths of the $2\nu_2$ and the hot-band slightly increase upon dilution with CO_2 (up to about 0.3 m.f.) reaching an ill-defined broad maximum in the 0.3–0.7 mole fraction range and decrease at higher concentration.

III. INTERPRETATION

All the vibrations studied in the binary mixture (induced and allowed in CS_2 and allowed in CO_2) display a peculiar trend with the CO_2 dilution in a common concentration range extending roughly between 0.3 and 0.7 mole fraction. It is in this concentration domain that the strong non-ideality of the binary mixture has been put in evidence by thermodynamic studies. Clearly, there is a correlation between the

spectral domain is quite complicated due to the overlap of the line corresponding to this transition with its hot-bands and also with the transitions lines of the different sulphur isotopic molecules of CS_2.[3] Nevertheless, this region can be nicely decomposed using for each transition a single Lorentzian profile as illustrated for a very diluted solution of CS_2 in CO_2 (x_{CO_2} = 0.94). This concentration which has been selected as carbon disulphide is expected to exist under monomeric forms allowing a comparison with the gas phase results reported by Montero *et al.*[3]

We found that, within experimental uncertainties, the values of the band centre of the fitted Lorentzian fully match the values of the vibrational transitions observed in gas phase, and thus allow assigning the two intense transitions to $2\nu_2$ and its hot-band according to these authors (see the supplementary material[117]). These two peaks have almost equal widths (about 6 cm^{-1}), an order of magnitude narrower than the ν_2 mode, indicating that the band-shaping mechanisms involved in these transitions differ from those conditioning the ν_2 mode. Indeed, due to the Fermi resonance phenomenon, $2\nu_2$ and its hot-band borrow their activity from the ν_1 mode. As a further consequence, it might also pointed out that these polarised profiles ($\rho \leq 0.1$), which are close to isotropic ones in view of the large depolarisation ratio of the two bands, are mostly sensitive to the vibrational (phase) relaxation processes.
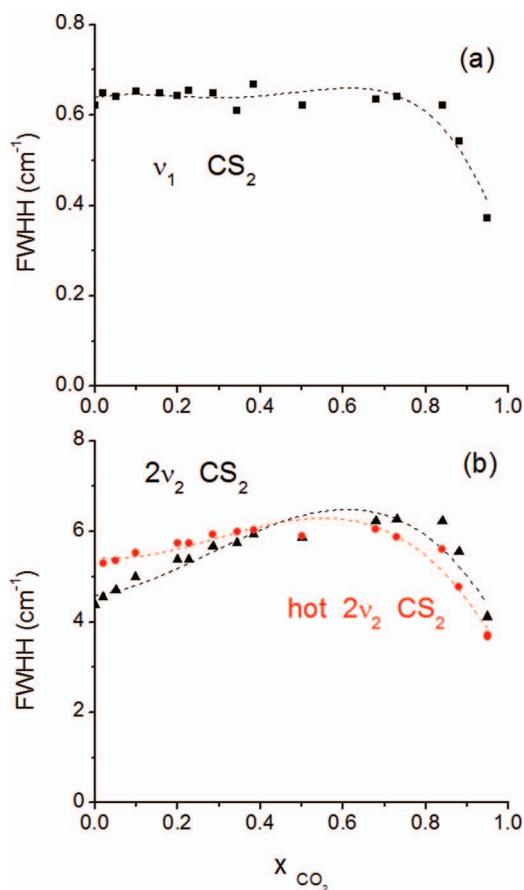

FIG. 12. Evolution of the FWHH of the ν_1 (a), $2\nu_2$, and its hot-band (b) of CS_2 with the CO_2 concentration at 313 K. The dashed lines obtained by fitting a third order polynomial are given to guide the eye.

molecular spectroscopic observables and the thermodynamic phenomenological approach.

A. Analysis of the induced modes of CS_2

We will consider binary mixtures concentrated in CS_2 ($x_{CO_2} \leq 0.5$) and ground our analysis on the studies of the induced spectra of CS_2 and CO_2 by Madden and co-workers.[18,21,23–29] This analysis is based on physical considerations due to the lack of detailed theoretical treatment on CI spectra of binary mixtures,[81] which, even available, has limited application because many molecular properties would be required and most of them are unknown.[28] In this theoretical framework, the Raman activity of the ν_2 and ν_3 modes is mainly due to a dipole-induced quadrupole interaction (A'-α) mechanism (see discussion in the supplementary material[117]). In this approach, the ν_2 and ν_3 modes have similar bandshape and constitute sensitive probes of the multi-body translational and rotational contributions in the interaction mechanisms. Therefore, the band shapes and the intensities of the profiles are expected to evolve upon dilution of CS_2 by CO_2. Surprisingly, this is not verified experimentally and interpreting these results using the CI theoretical framework seems *a priori* a difficult task. Indeed, the substitution of CS_2 by CO_2 molecules should reduce the intensity of the induced modes as CO_2 is less polarisable than CS_2 ($\alpha_{CS_2} = 9.7 \times 10^{-40}$ C^2 m^2 J^{-1} and $\alpha_{CO_2} = 3.24 \times 10^{-40}$ C^2 m^2 J^{-1}),[23] and because the proportion of CO_2 and CS_2 neighbours around a given CS_2 molecule is varied. Furthermore, the two and three body terms characterising the CS_2-CS_2 and CS_2-CO_2 contributions to the intensity are *a priori* not expected to be equal. The previous results may be understood in the CI theoretical framework if the dilution does not affect the local translational and orientational ordering probed by the induced modes on the time scales and distances involved in the interaction mechanisms. Therefore, the only way to interpret our data is to suppose that the local molecular arrangement existing around a tagged CS_2 molecule in the pure fluid remains the same upon mixing with CO_2 in a broad concentration range extending up to $x_{CO_2} \leq 0.5$. Such an interpretation provides a picture of the mixing process at the molecular level. At very low CO_2 concentration, the conventional view of mixing in which CO_2 molecules start filling the voids existing or formed in the liquid phase of CS_2 applies. As the CO_2 concentration is increased, the preservation of the local structure of CS_2 implies that the incoming new CO_2 molecules should be preferentially accommodated in the vicinity of the existing CO_2 molecules leading to the progressive formation of local aggregates of CO_2, which should co-exist with clusters of CS_2. The size of these clusters should be such that the CS_2 molecules retain a local ordering close to that existing in the pure fluid to lead to the observation of CI profiles keeping band-shapes similar to those of pure CS_2. Incidentally, femtosecond optical Kerr effect/Raman-induced Kerr effect studies of CS_2-long-chain n-alkane (n = 14, 16) mixtures have shown that isolated CS_2 "pockets" are present and that the non-ideality of the mixture results from local concentrations of solvent and solute varying within a macroscopic

volume.[84] Because, CI Raman band shapes are conditioned by two and three body interaction, we argue that such clusters should be constituted, at least by three CS_2 molecules. In a more "chemical view," one could translate this picture by arguing that oligomers (dimers, trimers) existing in pure CS_2 still exist in the binary mixtures, hence preserving the so-called two and three body view of the CI approach. Such a view should be valid up to fairly large concentration of CO_2, i.e., for equimolar mixture, which clearly departs from a dilute solution. Therefore, the mixing process should lead to a "nano-segregation-like" of the liquid phase but without leading to a phase separation. This situation corresponds to a first solvation regime, which is somehow governed by the packing of the CS_2 liquid phase. Considering the variation of the intensity of the ν_2 mode with the CO_2 concentration, we may tentatively explain the observed constant trend of the intensity on physical ground. The interaction induced activity of a mode results from fluctuations of the local structure from the average structure, which preserves the molecular inversion centre of the liquid. Therefore, the activity of the mode which is forbidden for a fully isotropic phase in which there is a perfect cancellation of multi-body terms involved in the intermolecular interaction (2, 3, and 4 bodies) becomes weakly allowed due to an imperfect cancellation of these terms. On this basis, we may expect that as CO_2 is diluted in CS_2, there is of course an increasing disorder in the liquid due to the formation of CO_2 aggregates, and therefore the scattering activity increases. Our line of reasoning closely follows that of Cox and Madden.[25] These authors found that upon dilution of carbonyl sulfide in CS_2 the intensity of the ν_2 mode was initially increasing with the solute (OCS) concentration although the solution polarisability was falling. They stated pictorially, that this situation arises because introducing "holes" in a liquid composed of centro-symmetric molecules increases the disorder. More technically, the introduction of "holes" reduces the amount of three body scattering which is cancelling the positive two-body contribution to the intensity. However, we note that in the present study, the introduction of "holes" corresponds to the creation of CO_2 aggregates, which disrupt at the molecular scale the isotropy of the CS_2 liquid phase. This view which corresponds to a "nano-segregation" of the binary mixture is clearly different from the picture of an "ideal" solution in which a randomised substitution of CS_2 by CO_2 molecules within the neighbouring shell around a tagged CS_2 molecule is supposed.

At higher CO_2 concentration ($x_{CO_2} > 0.7$) there is clearly a variation of the band-shape of the ν_2 profile (Fig. 8). These observations suggest that, as the CO_2 concentration increases, the CS_2 neighbours around a CS_2 molecule become progressively substituted by CO_2 and that the mixing process occurs. In the "chemical picture" referred above, this would indicate that the effect of the dilution is to "isolate" CS_2 dimers in CO_2 cages. Therefore, at high CO_2 concentration ($x_{CO_2} > 0.7$), another regime is reached which corresponds to the coexistence of a diversity of species comprising homo and hetero dimers of CS_2 in a "bath" of CO_2 monomers and dimers.

It would be relevant to have some insight on the typical time-scales of the different processes involved in the mixtures.

In spite of the lack of theoretical treatment, estimation can be made taking into account that the band shapes of the ν_2 mode in the mixture are close to that of pure CS_2. The longest time scale corresponds in the CI framework to the life-time of a pair of interacting CS_2 molecules which can be approximated by τ_{tr}, the two body translational correlation time. This correlation time deduced from the line broadening of the translational contribution obtained by Ikawa *et al.*[35] in pure CS_2 is about 3 ps (0.1 MPa and 295 K). This "life-time" should be considered as an upper-bound value of the life time of the CS_2 clusters.

B. Analysis of the Fermi resonance modes of CO_2 and CS_2

The Fermi resonance modes of CO_2 and CS_2 should provide further and consistent information. These bands being strongly polarised are essentially governed by the vibrational relaxation (pure dephasing) of the molecules and constitute probes of the inter-molecular interactions taking place in the binary mixtures on a picosecond time scale.

1. From band centre position

For an ideal mixture, the band centre position of a vibrational mode varies linearly with the CO_2 concentration between two extreme points corresponding to those measured for the pure compound and infinitely diluted in the mixture.[85,86] In a mean field approach,[87,88] the band centre position of the CO_2 modes should decrease on going from the pure CO_2 to CO_2 very diluted in CS_2, as the attractive interactions between CO_2 molecules are weaker than between CO_2 and CS_2. Of course, for CS_2 modes, the band centre positions should increase with the concentration of CO_2. These overall trends are verified but, as expected, sizeable deviation from the linearity is observed confirming that the mixture is not ideal (Figs. 3 and 11). The negative departures from the linearity observed on these five bands in CO_2 concentrated solutions ($x_{CO_2} > 0.5$) imply that the replacement in the neighbouring shell of a CO_2 by a CS_2 molecule leads to both a greater red-shift due a stronger attractive interaction and a departure from a purely random ordering resulting from the formation of a hetero-dimer. This physical picture is also valid for CO_2 homo-dimers but which should play a much minor role as indicated by the order of magnitude of the stabilisation energy of the homo versus hetero dimers (see Sec. IV). This interpretation is consistent with the speciation of CO_2 in the mixture ($x_{CO_2} > 0.5$) as discussed before.

In CS_2 concentrated mixture ($x_{CO_2} < 0.5$), the band centre positions of the CO_2 dyad exhibit a positive deviation suggesting that the strength of attractive forces becomes weaker which is consistent with the CS_2 and CO_2 clusters picture. Indeed, CO_2 is "expelled" from CS_2 which keeps a "liquid-like" structure, whereas CO_2 exhibits a more "gaseous" behaviour. This picture allows interpreting the linear trend of the CS_2 band centre positions by considering that it follows a linear variation with the mean density of the mixture, which decreases as the CO_2 concentration in the mixture increases. In

conclusion, the study of the Fermi resonance modes confirms the existence of the different solvation regimes and the interpretation at the molecular level of the non-ideal behaviour of the CO_2-CS_2 mixture reached from the analysis of the induced modes.

2. From bandshape

In our previous studies in pure CO_2,[76,77] we have shown that each peak of the Fermi dyad results from the overlap of two components, assigned to the so-called "free" (monomeric) CO_2 (at higher frequency) and to the transient homo-dimers. This type of analysis applied to binary mixtures of CO_2 in a variety of organic solvents[55,58,62,63] showed that an additional profile centred at lower frequency should be included in each dyad peak to take into account the presence of hetero-dimers. This type of treatment was applied to a very concentrated CO_2-CS_2 solution ($x_{CO_2} = 0.94$) by fitting each dyad peak with a weighted sum of three Lorentzian components. The comparison of the spectrum of the mixture decomposed that way with that of neat CO_2 fitted with two Lorentzian profiles is illustrated for the upper dyad component in Fig. 13. The two lines observed at higher frequency in the mixtures are in close correspondence with the two features observed in neat CO_2 and thus assigned to monomers and homo-dimers. The third component centred at lower frequency and absent in neat CO_2 is ascribed to CO_2-CS_2 hetero-dimer. The signature of such transient complexes has been also detected between the dyads components
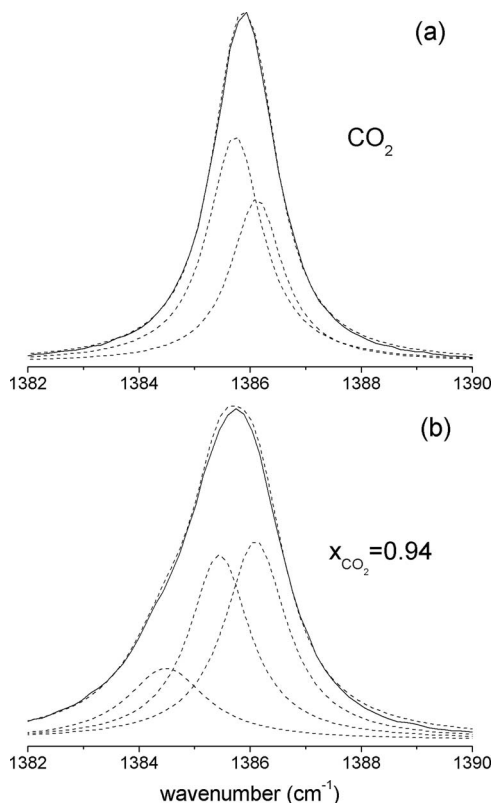

FIG. 13. Band-shape analysis of the I_{VV} profile of the upper component of the CO_2 Fermi dyad at 313 K of pure CO_2 ($\rho = 743.04$ kg m^{-3}, 13 MPa) (a) and of the more concentrated mixture ($x_{CO_2} = 0.94$, $\rho = 740$ kg m^{-3}) (b).
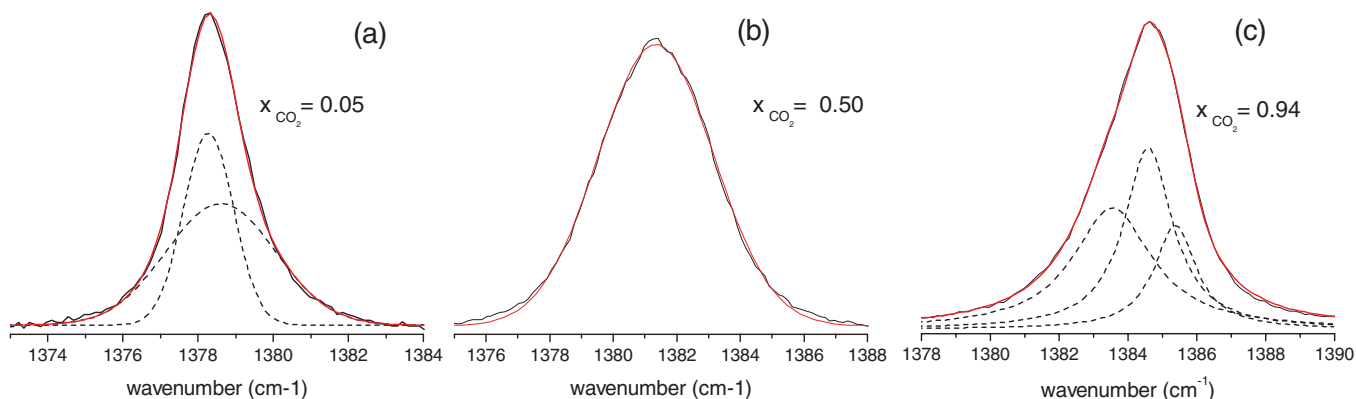
FIG. 14. Analysis of the band-shape of the I_{VV} profiles of the upper component of the CO_2 Fermi dyad at 313 K for different typical concentrations: two Gaussian profiles for concentrated mixture in CS_2 (a), a single Gaussian profile for equimolar concentration (b), and three Lorentzian profiles for CS_2 very diluted in CO_2 (c).

(see Sec. II B 1). Therefore, CO_2 is involved in three co-existing species (monomer, homo-dimer, and hetero-dimer) in highly concentrated solutions. However, this discrete speciation consistent with our previous studies could not be pursued in the entire concentration domain. Indeed, at equimolar concentration, the profiles of each component are well described by a single Gaussian (Fig. 14), whereas for more concentrated solutions in CS_2 two Gaussian profiles are needed. This diversity of description to follow the concentration dependence of the profiles reflects the existence of different solvation regimes as found before from the analysis of the CI profiles.

A good description of the profiles in the entire concentration domain will require a great number of components, and therefore there is the need to develop a chemical scheme with a set of several coupled chemical equilibrium equations involving CO_2 and CS_2 in different states of aggregation. Such an analysis requires the use of a large number of parameters and the knowledge of equilibrium constants.[89] Clearly, such an approach is more mathematically involved rather than providing a clear physical insight.

An important assumption in the previous treatments resides in the fact that they implicitly assume that the lifetime of the complex is greater than the Raman observation time leading to well defined bands associated with each characteristic species.[90,91] This hypothesis, supposing that the exchange dynamics of the species is in the so-called "slow exchange" regime, is certainly arguable when applied to transient short-lived complex. Indeed, the estimated life time of the CS_2 dimer is about 3 ps (as referred before), a value likely greater than that of the weaker hetero-dimer. If the hetero-dimer life time is less than 3 ps, the peaks associated to the CO_2-CS_2 hetero-dimer and CO_2 homo-dimer in the two sites could be separately observed, only if the band centres difference is greater than 1.8 cm^{-1}. In the previous band-shape treatment that difference is found to be about 1 cm^{-1} showing that a collapse of the peaks assigned to the two sites has already occurred. As a consequence, attempts to disentangle band-shape in terms of well-defined species may lead to arguable spectroscopic parameters extracted from fitting procedure, which assume that the chemical

slow-exchange limit applies. Besides, the use of a model taking into account the exchange dynamics is submitted to the same "technical limits" mentioned before consisting in the need to derive a chemical scheme with several coupled equations plus the need of using adjustable rate constants.

The description of the CS_2 Fermi resonance modes (ν_1, $2\nu_2$, and its hot band) using a single Lorentzian profile in the entire concentration domain allows inferring that the CS_2 molecule jumps between the two sites ("free" CS_2 and CS_2-CO_2 hetero-dimer) in the fast exchange regime.

IV. DISCUSSION ON THE NON-IDEAL BEHAVIOUR OF THE MIXTURE

For an ideal mixture composed of A and B molecules, the values of the homo (AA and BB) and hetero (AB) binary interaction energies (E) are of the same order of magnitude.[92] This means that the interchange energy $\Delta = 2E_{AB} - E_{AA} - E_{BB}$ is equal to zero. *Ab initio* calculations show that the order of magnitude of the stabilisation energy of the most stable CO_2 dimer (A), which is in a slipped configuration, is about -1.3 kcal mol^{-1}, whereas it is about -3.3 kcal mol^{-1} for a slipped CS_2 dimer (B) and intermediate for the CO_2-CS_2 slipped hetero-dimer (A-B about -1.7 kcal mol^{-1}).[93] The non-negligible value of Δ ($+1.2$ kcal mol^{-1}) confirms that the mixture is not ideal and the positive sign shows that CS_2 molecules are preferably surrounded by other CS_2 supporting a so-called quasi-chemical description of the solution energetic.[92] Incidentally, we note that even in the gaseous phase of pure CS_2, molecules tend to form highly symmetric clusters as the presence of dimers, trimers, and tetramers has been recently put in evidence by infrared spectroscopy in supersonic jet expansion of gas mixture of CS_2 in helium.[14–16]

Harsh-repulsive forces which govern the short range local ordering in liquids and contribute to the packing of CS_2 molecules via the molecular shape must play a relevant role in favouring the formation of clusters.[94] The free molecular volume[95] in pure CS_2 calculated from the molecular and van der Waals volumes[96] is about 28 Å^3, whereas it is about 38 Å^3 for CO_2. This estimation shows that CO_2 molecules hardly penetrate the CS_2 compact structure indicating that

a random mixing is un-favoured. Moreover, if the CO_2 molecule could be hosted in the structure of CS_2, it should occupy a smaller volume than its van der Waals one leading to shrinkage of the total volume in contradiction with the experimental volume additivity (see below).

The particular molecular shapes of CS_2 and CO_2, which can be modelled as hard-spherocylinders (HSC, cylinder of length L capped with half-spheres of diameter D at each extremity) with a shape anisotropy not very different (aspect ratio L/D = 0.87 and 0.76 for CS_2 and CO_2, respectively), should be taken into account (see discussion in the supplementary material[117]). Studies of bi-disperse HSC systems are scarce[97, 98] and devoted to higher values of molecular shape anisotropy than those of interest here. A number of studies have been devoted to HSC-Hard Sphere (HS) mixtures[99–103] in which a variety of micro-phases for a wide range of sphere sizes and concentration can exist. Microphase separation consisting in liquid-like region rich in either spheres or spherocylinders was observed.[101, 102] In a quite different context, investigations on jammed random packing of non-spherical granular matter have been also performed aimed at discussing the effect of shape and size of the particles on the packing density.[104–111] For mixtures of HS with HSC of the same diameter and with an HSC aspect ratio less than 1.3, it was shown that the mixture, which can be either in a segregated or in a dispersive state, always exhibits isochoric ideality.[109, 110]

The picture of the solvation in the mixture brought at the molecular level by spectroscopy may help in understanding the volumetric isothermal expansion ("swelling") of the CS_2 liquid phase. The swelling of the liquid phase of a molecular liquid upon injection of a gas under pressure is a thermodynamic observable of importance in chemical engineering studies.[112–116] To quantify the liquid phase swelling, we have calculated the evolution of the relative volume expansion $\Delta V/V$ of the liquid phase of CS_2 with the CO_2 concentration from the molar volumes v_m and v_{CS_2} of the mixture and pure CS_2, respectively.[116] The evolution of $\Delta V/V$ of the mixture closely follows the calculated $\Delta V/V = x_{CO_2} v_{CO_2}/(x_{CS_2} v_{CS_2})$ which is valid for an ideal mixture for which the volume additivity applies (see Fig. SI3 of the supplementary material[117]). Such a result, which leads to an apparent ideality of the mixture, might be interpreted at the molecular level by assuming that CS_2 and CO_2 are randomly mixed. However, such an interpretation is not correct and is contradicted by the experimental results and the previous analysis on molecular volumes considerations. As a matter of fact, the volume additivity is compatible with the picture of a segregated liquid phase as shown by mixtures of HS and HSC. Therefore, we conclude that the volume additivity is a necessary but not sufficient condition of ideality in agreement with the fact that this system exhibits a type II phase diagram. The existence of two solvation regimes with a plateau transition is appealing as providing further insight on the LLE phase diagram with a UCST at 290 K.[72, 73] Although at 313 K, the system is above the UCST, and thus, no demixing of the mixture occurs, it is still very close to the liquid-liquid critical point and the phase instability, although not macroscopically observable, is nevertheless still present at a molecular level.

V. CONCLUSION

The study of the Raman induced modes of CS_2 and of the Fermi resonance dyad of CO_2 and CS_2 shows that two solvation regimes are probed. The former is mainly of the "liquid-type" conditioned by the CS_2 liquid phase leading to a nano-segregation of the mixture from the pure liquid to equimolar dilution. The second regime, reached at higher CO_2 concentration ($x_{CO_2} > 0.7$) is "gaseous-like" and mostly controlled by the CO_2 involving a variety of species, such as CO_2 monomers and dimers, CO_2-CS_2 hetero dimers, likely exchanging on a picosecond time scale. This regime is close to that observed in mixtures of CO_2 with organic liquids. The transition between the two regimes takes place continuously in the range 0.3–0.7 m.f. and can be correlated with the plateau-like region observed on the pressure-composition diagram at 313 K (Fig. 1). Considerations on the interchange energy of the mixture and on the molecular volumes and shapes of the components allow showing that a subtle interplay between attractive and repulsive interactions condition the behaviour of this system reflected in the spectroscopic observables. This interplay allows rationalizing the observed volume additivity as a consequence of the nano-segregation of the liquid phase. It is in the ground of this interplay that the correlation between the two solvation regimes and the presence of the plateau-like region observed in the pressure-composition diagram has been rationalized.

As a final conclusion, we would like to emphasise on the ground of the present investigation that the CO_2-CS_2 liquid phase mixture constituted of highly symmetric molecules having similar shapes but differing by their charge distribution has a great interest to validate a number of important concepts in the domain of liquid state research. Experimental structural studies are also requested and could check the prediction coming out from the present investigation that the local ordering of CS_2 is almost unaffected upon a quite large dilution effect. In this context, quantum mechanical calculations aimed at investigating the structure of the CS_2-CO_2 clusters will be necessary. Theoretical efforts using MD will be of importance to understand the subtle balance between attractive and repulsive interactions, their spatial range and time scales in promoting a segregated phase at high CS_2 concentration smoothly evolving towards a more "homogeneous" liquid phase. These studies will also benefit from the field of Monte Carlo study aimed at investigating binary mixture of HSC having comparable aspect ratio also including attractive forces, a research area which is still in infancy. Finally the present study should provide an experimental basis for theoretical simulation in the domain of induced spectroscopy of binary mixtures of molecular liquids, which will enlarge the current knowledge already provided in this domain on the separate components of the mixture. Part of this work is currently under progress.[93]

ACKNOWLEDGMENTS

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[117]See supplementary material at http://dx.doi.org/10.1063/1.4821593 for detailed experimental conditions, asymmetry of the ν_2 mode of CS_2, analysis of the induced and $2\nu_2$ modes of CS_2, and non-ideal behaviour of the mixture.