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Infrared studies of CO₂ doped Xe solutions in gas, liquid and solid phases. The fundamental ν_3 band and the Coriolis perturbed Fermi doublet ($\nu_1 + \nu_2^1$, $\nu_1 + \nu_2^{11}$)

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Abstract

The IR absorption spectra of CO₂ doped Xe solutions have been recorded in the range of the fundamental $\nu_3(\Sigma_u)$ band and of the Coriolis perturbed $\nu_1 + \nu_2^1$, $\nu_1 + \nu_2^{11}(\pi_u)$ Fermi doublet ($\nu_1 + \nu_2 \approx 3\nu_2$) in gas, liquid and solid phases. The characteristic transformation and rapid narrowing of the ν_3 band, observed in the gas to liquid phase transition, shows marked hindering of the rotational motion of the CO₂ molecule in dense Xe mixtures. It was found that the liquid to solid phase transition is accompanied by noticeable broadening of the ν_3 band. The rotational motion of CO₂ is not frozen in solid Xe at least near the freezing point. This is in contrast with sharp narrowing of the vibrational bands and so with blocking up rotations in the case of a heavier CS₂ guest in the solid Xe host just below the freezing point. The intensity ratio $A(\nu_1 + \nu_2^1)/A(\nu_1 + \nu_2^{11})$ of the Coriolis perturbed $\nu_1 + \nu_2^1$, $\nu_1 + \nu_2^{11}$ doublet reveals the noticeable increase from 8 ± 1 in a low density gas to 18 ± 2 in the liquid phase. The results obtained suggest remarkable modification of the second-order Coriolis coupling in the case of CO₂ doped dense liquid Xe. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Vibrational spectra; CO₂; Noble gas solutions; Phase transition; Rotational relaxation processes; Coriolis coupling

1. Introduction

Molecular rotations and their perturbations play a crucial role in vibrational band-shape formation of simple molecules [1–4]. Infrared spectroscopy of vibrational bands of such molecules should search for evidence of a more or less hindered rotational motion in dense media. The Coriolis coupling often

modifies profiles of vibrational–rotational bands in the gas phase. Simultaneously, the intensity ratios of the coupled bands might suffer noticeable variation as compared with unperturbed states. The present paper reports phase transition effects on the strong, fundamental ν_3 band of CO₂ and on the weak $\nu_1 + \nu_2^1$, $\nu_1 + \nu_2^{11}$ Fermi doublet perturbed by the Σ_u modes (ν_3 , $\nu_1 + \nu_3$, etc.) due to the second-order Coriolis coupling. The IR spectra have been measured in gas, liquid and solid Xe solutions. The transformation of the band shape of ν_3 is treated in the framework of the simple orienting field model [5,6] in the case of the gas and liquid states. In the case of liquid to solid state transition, the Debye limit for J -diffusion of a linear

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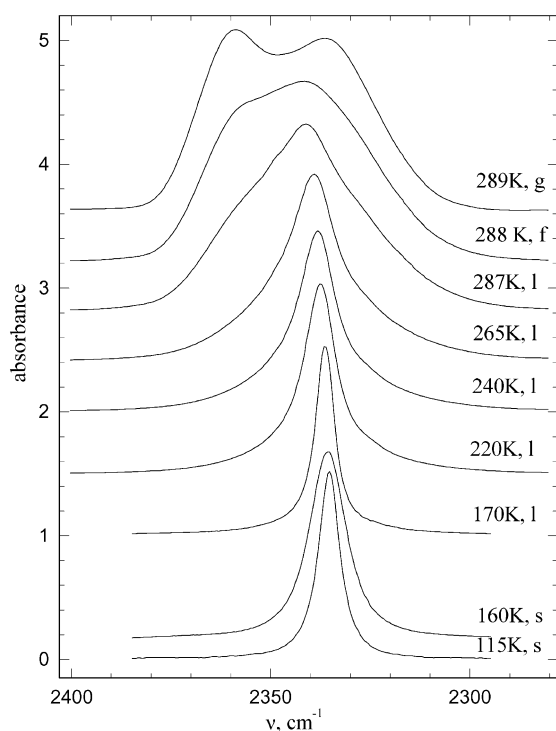


Fig. 1. Evolution of the ν_3 band of CO_2 in Xe. g: gas, f: fluid, l: liquid, and s: solid.

rotator [7] is applied. The intensity ratio, $A(\nu_1 + \nu_2^1)/A(\nu_1 + \nu_2^{11})$ of the $\nu_1 + \nu_2^1$, $\nu_1 + \nu_2^{11}$ doublet perturbed by the modes mentioned before, have been measured in the gas and liquid Xe mixtures.

2. Experimental

IR spectra of CO_2 doped Xe solutions were recorded on IFS-28 spectrometer (resolution $\sim 0.7 \text{ cm}^{-1}$). The gas, liquid and solid phase measurements have been performed in a homemade cryostat equipped with BaF_2 optics. Temperature of the sample was measured with an accuracy of 3 K. The concentration $n(\text{CO}_2)$ of CO_2 in liquid Xe solution was varied in the range of $\sim 10^{17}$ – 10^{20} molecules/ cm^3 . A lower concentration was used in studies of the shape of the ν_3 band. Higher concentrations were chosen for detection of weak $\nu_1 + \nu_2^1$ and $\nu_1 + \nu_2^{11}$ Fermi doublet ($\nu_1 + \nu_2 \approx 3\nu_2$). It should be noted that results of measurements of the intensity ratio $A(\nu_1 + \nu_2^1)/A(\nu_1 + \nu_2^{11})$

may suffer from induced ν_2 , ν_1^1 and ν_2 , ν_1^{11} bands ($\nu_1 \approx 2\nu_2$) when using higher concentrations $n(\text{CO}_2) > 5 \times 10^{20}$ molecules/ cm^3 .

Gas phase spectra at $T \sim 290$ – 270 K were studied first. Then, by pressuring Xe and by slow cooling, the sample was transferred into the fluid and liquid states. The vibrational bands of a liquid were monitored at $T \sim 280$ – 168 K. After that, by slow cooling below, the melting point (~ 165 K), the transparent solid sample was grown from the liquid as described previously in Ref. [8]. The solid sample was studied at $T \sim 162$ – 90 K.

3. Results and discussion

3.1. The fundamental $\nu_3(\Sigma_u^-)$ band of CO_2

Fig. 1 presents evolution of the ν_3 band shape of CO_2 in Xe when going from gas to liquid and then to solid state. The gas phase band is the typical doublet with the central minimum between R and P branches of that vibrational–rotational band. Density growth of the fluid results in disappearance of the minimum. In the liquid state, the band becomes a singlet-like shaped, with remnants of R and P branches on its high and low frequency shoulders. When going to lower temperature of the liquid, the band narrows rapidly. It becomes almost symmetric Lorentz-like at the lowest temperature of the liquid ($T < 170$ K).

The liquid to solid phase transition gives no sharp changes of the profile of the ν_3 band. It looks exactly symmetric and is characterized by Voigt-like profile, with Lorentz part dominating. The band is somewhat broader just after freezing than it is in the liquid before freezing. Nevertheless, temperature lowering results in narrowing of the ν_3 band in the solid. As a result, the band becomes as narrow as it is in the liquid near the freezing point at the lowest temperature of the solid ($T_{\min} \sim 90$ K).

The results obtained are interpreted in the framework of a simple orienting field model of molecular rotation. The model takes account of the appearance of the local ordering of molecular neighbors in the liquid state. The full description of the model can be found in Refs. [5,6,9]. Briefly, the ordering effect is modeled by introducing the effective orienting field of

Table 1

Estimated values of the reduced angular momentum correlation time τ_J^* for the ν_3 band of CO₂ in Xe

A	T (K)	$\rho \times 10^{-22}$ (molecules/cm ³)	2Γ (cm ⁻¹)	$2\Gamma_G$ (cm ⁻¹)	$2\Gamma_L$ (cm ⁻¹)	ν_J (cm ⁻¹)	U_0 (K)	$\tau_J \times 10^{12}$ (s)	τ_J^*
Xe (s)	100	1.57	6.1	1.7	5.6	39	~ 0	0.14	0.27
Xe (s)	160	1.57	11.2	3.9	9.6	36	~ 0	0.15	0.37
Xe (l)	166	1.39	5.7	~ 0	5.7	~ 40	8×10^2	0.13	0.33
Xe (l)	220	1.2	10.4	–	–	16	8×10^2	0.33	0.96
Xe (l)	265	0.99	–	–	–	15	6×10^2	0.35	1.1
Xe (g)	289	~ 0.1	–	–	–	7	1×10^2	0.76	2.5

axial symmetry. The following simple potential function is chosen for homonuclear molecules:

$$U(\cos \alpha) = -U_0 \cos^2 \alpha, \quad (1)$$

where α is the angle between molecular axis and the field direction, U_0 is the height of the hindering barrier. The relaxation process in the system, including the CO₂ molecule and the nearest

environment, is considered as a Poisson sequence of sudden fluctuations with mean frequency ν_J . In the case of $U_0 = 0$, the orienting field model is reduced to the known model of diffusion of the molecular angular momentum J (so called J -diffusion model).

The model gives the classical value of the correlation function $C(t)$ of the vibrational transition dipole moment of the molecule and then the spectral density function $A(\omega)$ of a band:

$$A(\omega) = \pi^{-1} \text{Re } \hat{C}(\omega), \quad (2)$$

where ω is a frequency displacement from the band origin. The parameters U_0 and ν_J can be estimated by fitting the calculated profiles $A(\omega)$ to the symmetrized experimental band shapes: $A_s^{\text{exp}}(\omega) = 0.5(A^{\text{exp}}(\omega) + A^{\text{exp}}(-\omega))$. The evaluated values of the model parameters U_0 and ν_J are presented in Table 1. The density ρ of Xe solvent, the width at half maximum 2Γ for registered singlet-like bands, the Lorentz $2\Gamma_L$ and the Gauss $2\Gamma_G$ parts of the width of the bands approximated by the Voigt profile, the angular momentum correlation time $\tau_J \equiv 1/(2\pi c\nu_J)$ and the reduced angular momentum correlation time $\tau_J^* \equiv 2\pi\mu_2^{1/2}\tau_J$ are also given in Table 1. Here c is the velocity of light, μ_2 is the second spectral moment of the band. The τ_J^* value can be considered as a mean part of the unperturbed rotation period of CO₂ between two consequent fluctuations. Note that the barrier increases rapidly when going to a denser liquid state. Simultaneously, the τ_J^* value decreases from ~2 to ~0.3. In the framework of the model, the liquid to solid phase transition results in a noticeable decrease of hindering just below the freezing point. A higher symmetry of the site occupied by the relatively small CO₂ guest may favor a lower perturbation

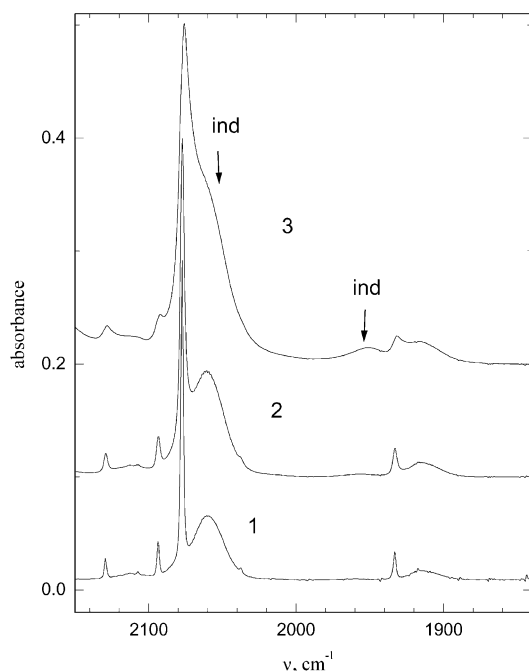


Fig. 2. Region of the weak $\nu_1 + \nu_2^1$ and $\nu_1 + \nu_2^{11}$ Fermi doublet in the gas phase. $T = 290$ K, the positions of the induced bands are shown by arrows: (1) $\rho(\text{CO}_2) \sim 6$ amagat, (2) $\rho(\text{CO}_2) \sim 18$ amagat, (3) $\rho(\text{CO}_2) \sim 36$ amagat; spectra 2 and 3 are scaled by factors 3 and 6, respectively. Small peaks on the high frequency side of the spectra belong to hot transitions.

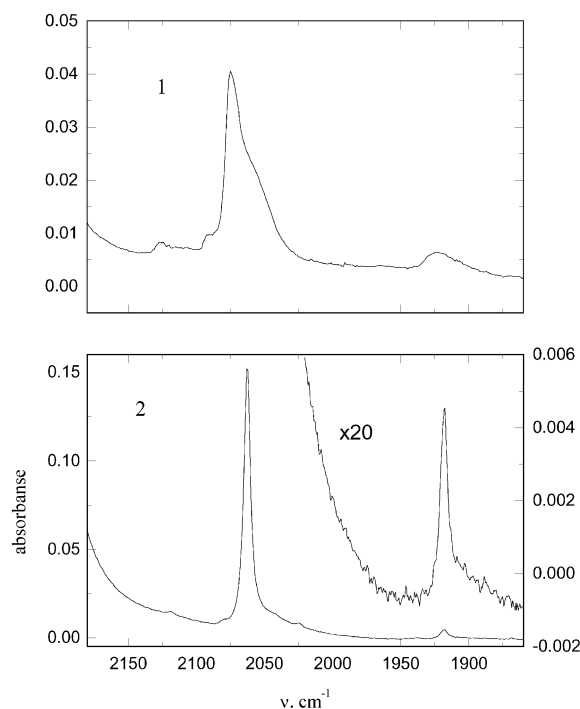


Fig. 3. The $\nu_1 + \nu_2^1$, $\nu_1 + \nu_2^{11}$ Fermi doublet of CO₂ in Xe. $n(\text{CO}_2) \sim 5 \times 10^{19}$ molecules/cm³; (1) gas phase, $\rho(\text{Xe}) \sim 40$ amagat; $T \sim 290$ K; (2) liquid phase, $\rho(\text{Xe}) \sim 350$ amagat, $T \sim 190$ K. Small peaks on the high frequency side of the spectra belong to hot transitions.

of molecular rotation in the face-centered cube solid Xe host. In any case, one can claim that the rotational motion of CO₂ is not blocked up in the solid Xe host. The results obtained are close to that predicted by the Debye model of rotational diffusion. The τ_j^* value decreases when going to a lower temperature of the solid, i.e. the rotation becomes more hindered in the low temperature solid Xe host.

The data for CO₂ guest in Xe solid host are contrasted with that obtained for neat solid CO₂. In the case of the neat CO₂ sample, the rotation is frozen just below the freezing point (~ 210 K). At last, our previous measurements suggest blocking up rotations of a heavier CS₂ linear rotator in the solid Xe host. Indeed, the width of the ν_3 band of CS₂ shows sharp narrowing from $2\Gamma \sim 1.7$ cm⁻¹ at liquid state near the melting point to $2\Gamma < 0.5$ cm⁻¹ just below the freezing point of the Xe host. Steric arguments seem to be preferable in the last case of a larger CS₂.

3.2. The Fermi $\nu_1 + \nu_2^1$, $\nu_1 + \nu_2^{11}(\pi_u)$ doublet

These weak bands originate from π_u (11^10), (03^10) states of CO₂ being in Fermi resonance. Additionally, they are disturbed by the Σ_u modes (ν_3 , $\nu_1 + \nu_3$, etc.) due to the second-order Coriolis coupling. Also, the induced ν_1 , ν_2^1 and ν_1 , ν_2^{11} bands corresponding to simultaneous excitation of (01^10), (100) and (01^10), (02^00) states of the interacting molecular pair are present in the same frequency region. In the case of a higher concentration of CO₂, they can overlap with the studied Fermi doublet, as shown in Fig. 2 for the case of gaseous CO₂. These induced bands become about two orders more intense than the weak Coriolis perturbed doublet in the net CO₂ liquid. At a smaller concentration of CO₂, the overlapping effect may result in some overestimation of the intensity of the high frequency $\nu_1 + \nu_2^1$ component of the weak doublet. Therefore, the quantitative measurements of the intensities of these weak π_u bands should be performed in dilute solutions with relatively small content of CO₂. Fig. 3 displays results of the registration of this Fermi doublet in Xe mixtures in the gas (upper spectrum) and in the low temperature liquid state (lower spectrum). If one takes account of the second-order Coriolis coupling, then one can obtain for the intensity ratio $A(\nu_1 + \nu_2^1)/A(\nu_1 + \nu_2^{11})$:

$$\left(\frac{A_I}{A_{II}}\right)_{\text{Cor}} = \left(\frac{A_I}{A_{II}}\right)_{\text{vib}} \frac{1 + 2\xi_I + (\xi_I kT/2Bhc)}{1 + 2\xi_{II} + (\xi_{II} kT/2Bhc)}, \quad (3)$$

where $(A_I + A_{II})_{\text{vib}} \equiv A(\nu_1 + \nu_2^1)/A(\nu_1 + \nu_2^{11})_{\text{vib}}$ is the intensity ratio for the vibrational intensities of the high frequency $\nu_1 + \nu_2^1$ and low frequency $\nu_1 + \nu_2^{11}$ components of the Fermi doublet, according to Ref. [10], $(A_I/A_{II})_{\text{vib}}^{\text{gas}} = 12.13$ in the gas phase; $\xi_I = -0.0373$ [11], $\xi_{II} = -0.0598$ [12] are the Coriolis interaction coefficients, $B = 0.39$ cm⁻¹ [13] is the rotational constant. Eq. (3) gives $(A_I/A_{II})_{\text{Cor}}^{\text{gas}} = 8.7$ at $T \sim 290$ K. The experimental value is 8 ± 1 . Due to the sharpening of Fermi resonance, the intensity ratio should increase up to $(A_I/A_{II})_{\text{vib}}^{\text{Xe}} \sim 19$ [14] in liquid Xe. Taking account of the Coriolis disturbance, one can obtain from Eq. (3) $(A_I/A_{II})_{\text{Cor}}^{\text{Xe}} \sim 15$ at $T \sim 190$ K. The experimental value is 18 ± 2 . Simultaneously, there is observed marked decrease of low frequency shoulders of these π_u bands, which could not be fully explained by a depopulation of higher

rotational states at a lower temperature of the liquid Xe.

It seems to be reasonable to suggest that both effects observed show noticeable modification of the second-order Coriolis coupling in the case of dense liquid Xe solution. Stronger effects could be expected in the solid Xe. We failed to measure the intensity ratio (A_I/A_{II}) in the solid. It is due to a smaller solubility of CO₂ in the solid Xe host. Appropriate measurements may be performed if one could prepare a longer crystal sample.

4. Conclusions

The transformation of the ν_3 band shape of CO₂ has been studied in CO₂ + Xe mixtures at gas to liquid and at liquid to solid phase transitions. The analysis performed in the framework of the orienting field model shows rapid growth of hindering of rotation motion of CO₂ guest in Xe host while going from gas to dense liquid state. The liquid to solid phase transition reveals the noticeable broadening of the ν_3 band of CO₂ guest in Xe host. This result contrasts with the sharp narrowing of the ν_3 band of a heavier CS₂ molecule, which is observed just below the freezing point of Xe.

The weak Coriolis perturbed $\nu_1 + \nu_2^1$, $\nu_1 + \nu_2^{11}$ Fermi doublet of CO₂ guest has been registered in gas and in liquid Xe host. The intensity ratio (A_I/A_{II}) was estimated. The noticeable growth of the ratio from 8 ± 1 to 18 ± 2 has been revealed at gas to liquid state transition. The effect shows remarkable modification of the second-order Coriolis coupling for CO₂ guest in low temperature dense Xe host.

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