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Indication for a change of dynamics in plastic crystal chloroadamantane: Raman scattering experiment and molecular dynamics simulation

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Abstract

Raman scattering experiment and molecular dynamics simulation have been performed on orientationally disordered crystal chloroadamantane. This investigation shows clear indication for a change of vibrational dynamics in the frequency range (2 cm^{-1} – 230 cm^{-1}) at the temperature T_x corresponding to the onset of non-exponential relaxation and consistent with previous NMR and MD studies. This allows us to support the existence of a 'landscape-influenced' regime above the critical temperature T_c of the mode coupling theory. Convincing experimental evidence of local orientational ordering which can be nicely probed from the so-called bending mode of the chloroadamantane molecule are also given.

1. Introduction

It is now well established that the phenomenology of glass formation is also displayed by some partially disordered molecular crystals called *plastic* in which the average position of the centres of mass are ordered on a lattice while the orientations are dynamically disordered. Indeed, some of them, called *glassy crystals* [1], such as cyanoadamantane (CNa) [2], ethanol [3, 4], cyclooctanol [5] or difluorotetrachloroethane [6] can be deeply supercooled and present many properties characteristic of the conventional molecular liquid glasses such as a step in the specific heat at the glass transition or a non-Arrhenius behavior of the relaxation times. Those compounds have led recently to a strong interest since they offer valuable possibilities to focus mainly on the role of the orientational degrees of freedom (ODOF) of which the importance during the glass formation remains a matter of debate at present. It has to be noticed that glassy crystals in opposition to the so called 'orientational glasses' like mixed crystals $\text{Ar}_{1-x}(\text{N}_2)_x$ or $(\text{KCN})_x(\text{KBr})_{1-x}$ are not frustrated by quenched disorder externally imposed by a dilution [7].

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In addition to the calorimetric glass transition observed at the temperature T_g [8], much attention has been devoted in the past ten years to the existence of several dynamical transitions which could occur above T_g in glass forming liquids. The mode coupling theory (MCT) [9] particularly predicts that a dynamical decoupling occurs at a critical temperature $T_c > T_g$. Many of the predictions of MCT, which initially described simple van der Waals atomic liquids, has been also confirmed by molecular dynamics (MD) simulations [10–12] and experiments [13–17] for real molecular liquid glass formers. It is now well accepted that T_c also marks the crossover to the ‘landscape dominated’ regime, as advocated a long time ago by Goldstein [18], where dynamics can be described as thermally activated hoppings between inherent structures (minima of the potential energy). It has also been demonstrated that another remarkable crossover temperature T_x can be identified above T_c which coincides with the onset of non-exponential relaxation i.e. the ‘landscape influenced’ regime [19–21]. However, the precise nature of this second crossover remains at present unclear.

Very recently, we have found chloroadamantane $C_{10}H_{15}Cl$ (Cla) to be a very favourable and relevant system to investigate rotational dynamics in the pico-nanosecond regime in the temperature range close to $[T_c, T_x]$. This compound shows a plastic phase over a wide interval of temperature [244–442] K and a structure isomorphous to CNa [22]. To our knowledge, no glass transition has been observed in Cla. By means of MD simulation, we have particularly shown that MCT gives a good description of dynamics and that dynamical crossover temperatures $T_c \simeq 225$ K and $T_x \simeq 350$ K could be extracted both in the α and β relaxational regimes [23,24]. These results were confirmed by NMR experiments [23] where T_x was found close to 330 K. It should be noted that a calorimetric anomaly was also reported by Oguni *et al* [25] in the plastic phase of Cla. The evolution of the specific heat C_p shows clearly an anomalous hump which covers the entire temperature range where the dynamical crossover is seen in our NMR and MD investigation at T_x [23]. We interpreted qualitatively its origin as an abrupt change in curvature of the entropy versus temperature evolution due to the strong localization of the dipole along the crystal directions.

The aim of this paper is to present and discuss new results obtained on Cla by Raman scattering experiment and MD simulation. Vibrational dynamics of this compound have been particularly investigated in the frequency range (2 cm^{-1} – 230 cm^{-1}). Convincing experimental and numerical evidence confirm the existence of a dynamical crossover occurring at $T_x \simeq 330$ K (350 K for MD simulation) in the rotator phase of Cla. It will be shown that the change in the nature of the dynamics i.e. the onset of non-exponential relaxation, is closely associated to a local ordering of the dipolar order which can be nicely probed from the so-called bending mode of the Cla molecule.

2. Experimental details

Non-polarized Raman experiments were carried out on a powder sample sealed into a spherical glass container. The spectra of Cla covering the frequency range from 2 to 230 cm^{-1} , were taken with an XY Dilor spectrometer in the back-scattering geometry, using a mixed Argon–Krypton Coherent laser operating at 647.1 nm. The Dilor spectrometer is composed of a double monochromator comprising four mirrors characterized by a focal length of 800 mm, and a spectrograph. The entrance and exit slits are opened to $100\ \mu\text{m}$, determining the incident radiation a resolution nearly less than 1 cm^{-1} in the low-frequency range. It is the monochromator which prohibits the exciting line from entering the spectrograph field. The well-adapted positioning of the monochromator with respect to the spectrograph and the choice of experimental conditions (incident radiation, slit width) allow a rejection of the exciting light down to 2 cm^{-1} . Low-temperature investigations were performed both in the ordered and

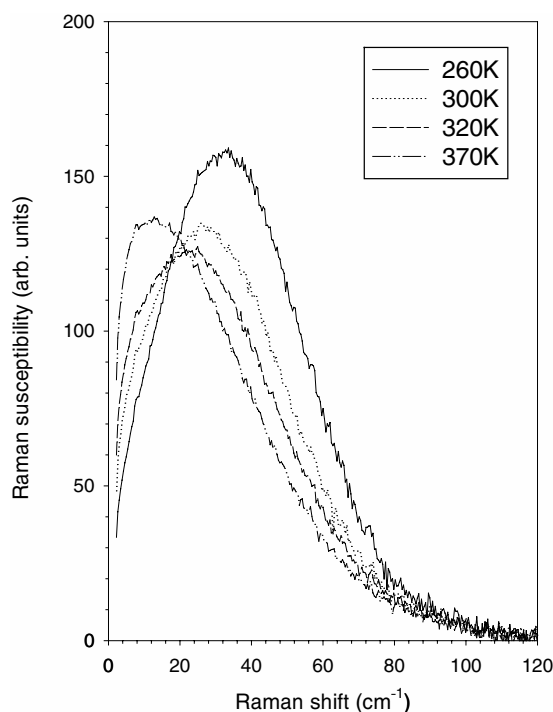


Figure 1. Temperature dependence of the low-frequency Raman susceptibility $\chi''(\omega)$.

plastic phases using an Oxford nitrogen-flux device, whereas high temperature measurements are made with a compressed hot-airstream system. The overlapping of the low- (200 K–320 K) and high- (310 K–370 K) temperature ranges, allows us to rescale accurately the temperature dependences of the Raman spectra obtained with the two different temperature devices.

3. Results and discussion

The Raman spectrum of the plastic phase of Cla in the (2 cm^{-1} – 230 cm^{-1}) frequency range is composed of two distinctive parts, which are separately analysed:

- the low-frequency Raman spectrum corresponding to the (2 cm^{-1} – 120 cm^{-1}),
- and a Raman band around 215 cm^{-1} , assigned to the angular distortion of the C–Cl bond with respect to the C_3 molecular axis i.e. the so-called bending mode,

3.1. Temperature dependence of the low-frequency Raman spectrum of Cla in the plastic phase

In order to get a better insight of spectral details in the very low-frequency range of disordered systems, the Raman intensity $I(\omega)$ is usually converted in Raman susceptibility, according to:

$$\chi''(\omega) = \frac{I(\omega)}{n(\omega) + 1}$$

where $[n(\omega) + 1]$ is the Bose occupation number. The temperature dependence of the low-frequency Raman susceptibility is plotted in figure 1. At the lowest temperature investigated

in the plastic phase of Cl_a ($T = 260$ K), the low-frequency Raman susceptibility (see figure 1) resembles the phonon density of states dominated by a broad feature, and thus exhibits a lineshape characteristic of a highly disordered system as expected for a plastic phase. A more accurate investigation of the low-frequency range using a fitting procedure reveals that the broad Raman band around 40 cm^{-1} is composed of a double hump structure with two maxima around 20 cm^{-1} and 40 cm^{-1} . The best result is obtained using a gaussian and a lognormal shapes for respectively the low- and high-frequency components as reported in figure 2

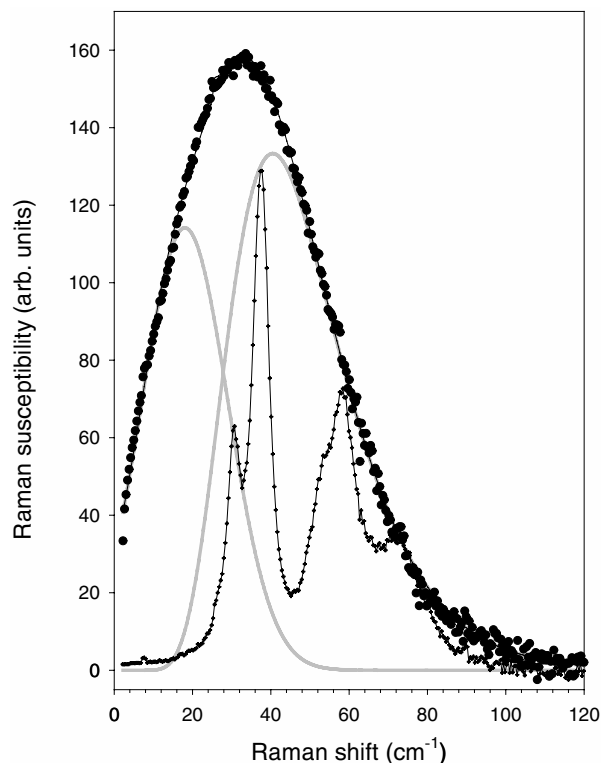


Figure 2. Low-frequency Raman susceptibility $\chi''(\omega)$ as function of the frequency at the temperature $T = 260$ K (points). The lineshape is fitted using a gaussian and a lognormal shapes for respectively the low- and high-frequency components (solid grey lines). The lognormal shape appears rigorously as the envelope of the low-frequency phonon peaks of the ordered phase (small points, the line is guide for the eye).

(i) The high-frequency component appears rigorously as the envelope of the low-frequency phonon peaks of the ordered phase and thus can be interpreted as resulting from an inhomogeneous broadening of the lattice modes of the ordered phase. Raman investigations carried out in the plastic phase of CNa [26] have revealed the existence of such an envelope that mirrors the density of states of librational motions around the C_3 molecular axes in the plastic phase. The close relationship between the two plastic phase structures suggests that the broad high-frequency contribution of the low-frequency Raman spectrum corresponds to a distribution of molecular surroundings. The best description of this density of librational states by a lognormal curve can be considered as indicative of a description of the plastic phase in terms of a non-continuous disordered structure, because such a lognormal function is generally used to fit the shape of the boson peak [27] in molecular glass-forming [28], inorganic

glasses [29], polymers [30, 31], and nanostructures [32]. Since the boson peak is classically associated to heterogeneous structures, the broad lognormal shape can be considered as the Raman signature of dynamical heterogeneities in the plastic phase.

(ii) Unlikely to the lognormal contribution, the low-frequency component has no correspondence in the Raman spectrum of the ordered phase. Consequently, this component should be necessarily assigned to reorientational molecular motions characteristic of the disorder in the plastic phase. It should be noted that previous neutron [33], dielectric [34] and NMR [23] studies have shown that large tumblings of the molecular C_3 axis among six fourfold crystallographic axes along the (100) directions occur in the rotator phase of Cl_a. The best representation of this low-frequency Raman intensity by a gaussian shape suggests that this intensity is representative of a statistical distribution of reorientation times. The temperature dependence of the FWHM of the low-frequency band confirms (see figure 3) that this band is not connected to anharmonic vibrations, and reveals that the distribution of reorientation times sharpens by temperature increasing.

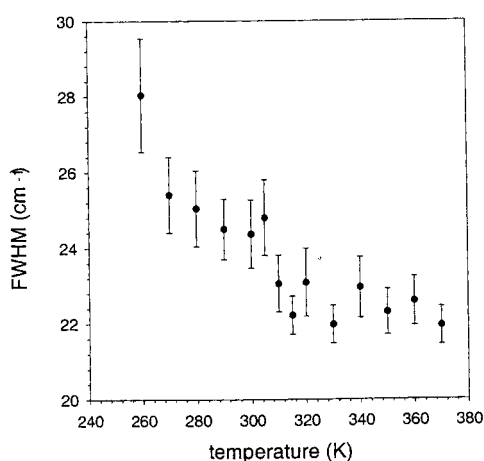


Figure 3. Temperature dependence of the FWHM of the lowest frequency band.

When increasing the temperature, the Raman susceptibility of the lognormal component seems to decrease whereas a concomitant increase of the low-frequency component is observed. This observation can be confirmed, and more carefully investigated by plotting the Raman susceptibility at the maximum of the two components with temperature increasing (see figure 4). It is clearly observed that the Raman susceptibility of the lognormal component decreases from 300 K, whereas the susceptibility of the low-frequency component slightly increases from 330 K. The temperature dependence of the two components of the broad low-frequency band, determined from the fitting procedure previously described, is plotted in figure 5 and reveals a slight change of slope at 330 K close to the NMR and MD simulation crossover temperature T_x [23, 24].

3.2. Investigations in the (200 cm^{-1} – 230 cm^{-1}) spectral range

In the bending mode region, a single Raman band is observed in the plastic phase around 214 cm^{-1} , and is fairly well fitted using a single damped oscillator. However, it appears slightly tailed in the high frequency side, in the low-temperature range of the plastic phase (see

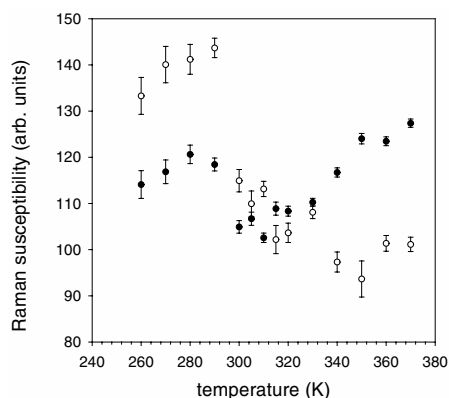


Figure 4. Maximum of the gaussian (full circle) and the lognormal (open circle) shapes used to fit the low-frequency Raman susceptibility $\chi''(\omega)$.

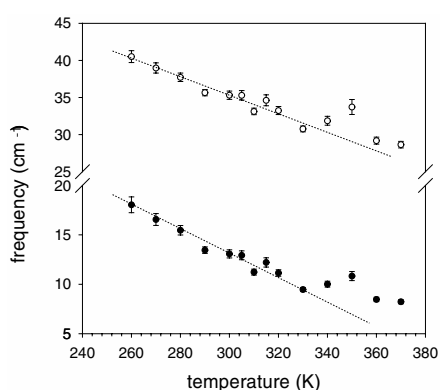


Figure 5. Temperature dependence of the gaussian (full circle) and lognormal (open circle) components of the broad low-frequency band. The dotted lines are guide for the eye.

figure 6). In the ordered phase, the molecular bending mode is split into three Raman active components because of a lower symmetry than in the plastic phase. The degeneracy of the C-Cl distortion with respect to the molecular axis can be correlated to a different local dipolar order. The asymmetry of bending mode in the plastic phase can be assigned as corresponding to the higher-frequency component observed in the low-temperature phase. Consequently the asymmetric lineshape in the plastic phase can be interpreted from the consideration of a local order, reminiscent of the ordered phase, in the disordered phase. Taking into account the nature of the bending mode, this local order should be characterized by a distribution of C_3 -axis orientation surroundings, that generates an inhomogeneous broadening of the bending mode.

Increasing the temperature, it is clearly observed from a fitting procedure, that the bending mode sharpens (see figure 7) between 260 K and 310 K, whereas by a further heating above 330 K, the Raman band broadens as can be expected in the frame of a usual temperature behaviour for a Raman band. A careful observation of the figure 6 reveals that the sharpness of the bending mode seems to correspond to a decrease of the tail. This clearly proves that local dipolar order vanishes because of the dynamical disorder. This latter can be considered as responsible for the drastic broadening of the bending mode above 330 K. A

very weak temperature dependence of the bending mode is observed up to 330 K, whereas above this temperature, this mode becomes clearly temperature independent. This behaviour can be interpreted by the disappearance of correlations between C_3 -axis orientations between neighbouring molecules. It can be assumed that above 330 K a change in the description of dynamical processes is observed as already seen in the low frequency range.

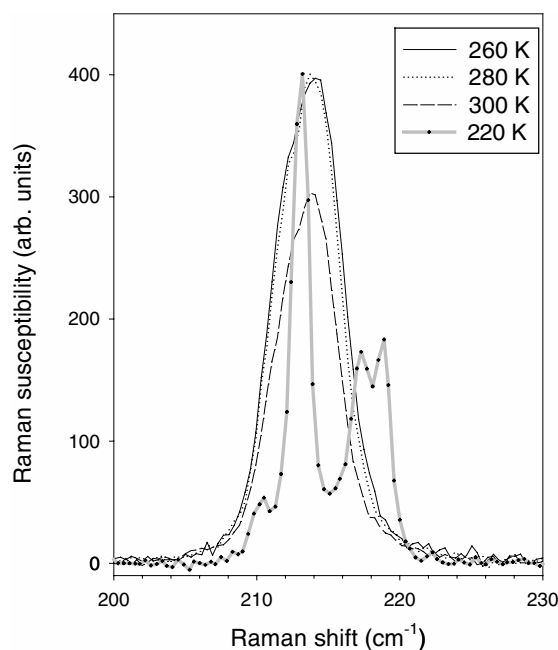


Figure 6. Bending mode of Cl_a at $\omega \simeq 214 \text{ cm}^{-1}$ at the temperatures 260, 280 and 300 K in the plastic phase and at 220 K in the ordered monoclinic phase (grey line).

In the plastic phase of CNa, this tail appears more pronounced [26,35], and the E molecular bending mode is also observed to be split into two Raman active components of A_g and B_g symmetry in the low-temperature phase. The symmetry assignment of the two bands was extracted from the evolution of their intensities in different polarizations with respect to those of the lattice modes. It was clearly demonstrated that these two contributions correspond to librations in and out-of the plane defined by the (a, b) crystallographic axes. The strong asymmetry of the bending mode in the plastic phase of CNa with regard to the one of Cl_a can be explained by the prominent part of the C–C–N protuberance in the orientational configurations of CNa molecules, and the correlated orientational disorder. Consequently, this internal mode can be considered as a very sensitive probe of the orientational disorder in the substituted adamantane family.

4. Molecular dynamics simulation

4.1. Model and details of the simulation

MD simulations of orientationally disordered molecular crystal Cl_a have been performed on a system of $N = 256$ ($4 \times 4 \times 4$ fcc crystalline cells) molecules interacting through a short range site–site Lennard-Jones potential. The model is completely described in [23,24,36], so only the essential details are given here. Modelled molecules are composed of two sites: one chlorine

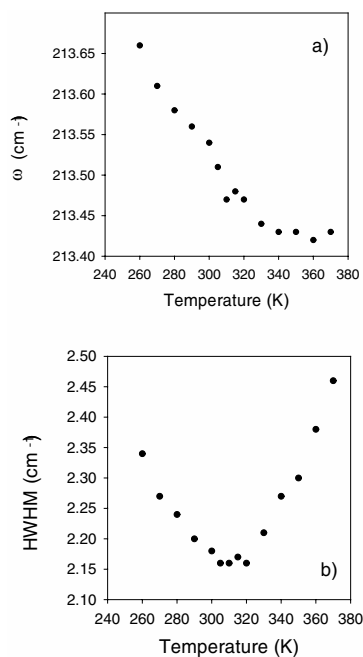


Figure 7. Temperature dependence of the frequency (a) and HWHM (b) of the bending mode in the plastic phase of Cla.

and one super atom that models the adamantane group $C_{10}H_{15}$. The electrostatic interactions were handled by the Ewald method with two partial charges ($q = \pm 0.151 e$) localized on both sites which reproduce the experimental dipolar moment $|\vec{\mu}| \simeq 2.39$ Debyes [34]. A time step of $\Delta t = 5$ fs was used to integrate the Newton's equations of motion. We worked in the NPT statistical ensemble with periodic boundary conditions. Plastic Cla has been investigated at 29 different temperatures from $T = 220$ to 500 K. Owing to the very long MD runs, equilibrium of the system could not be obtained below $T \simeq 220$ K.

4.2. Results

Motivated by the availability of extensive experimental data, we have carried out an MD simulation investigation in order to visualize clearly the molecular motions involved in the low frequency range and to achieve a microscopic interpretation of the experimental features.

The reorientational motions can be described by a set of correlation functions which are defined as [23, 37]:

$$C_l(t) = \langle P_l [\vec{\mu}(t) \cdot \vec{\mu}(0)] \rangle$$

where P_l is the l -order Legendre polynomial and $\vec{\mu}$ is the individual dipolar moment. Furthermore, the τ_1 and τ_2 correlation times are defined as the time it takes for their respective time correlation functions $C_{l=1,2}(t)$ to decay e^{-1} of their initial values. For uncorrelated small angular steps motion, it can be shown that the orientation correlation functions follow an exponential decay $C_l = \exp[-l(l+1)D_r t]$ where D_r is the rotational diffusion coefficient. This latter can be directly obtained from the time integral of the angular velocity correlation function $\langle \vec{\omega}(t) \cdot \vec{\omega}(0) \rangle$ [38]. Rotational diffusion coefficient D_r and relaxational times τ_l have been extracted from the simulation data and $l(l+1)D_r \cdot \tau_l$ is displayed for $l = 1$ and 2 in

figure 8. Below $T_x \simeq 350$ K, we observe clearly that $l(l+1)D_r \cdot \tau_l$ deviate from unity. This result proves that non-exponential relaxations occur below T_x and confirms the dynamical crossover already detected in [23, 24]. It also shows that below this temperature the relation $\tau_1/\tau_2 \simeq 3$ corresponding to free small-step rotation diffusion is not granted as seen in molecular liquid glass formers [11, 12, 39].

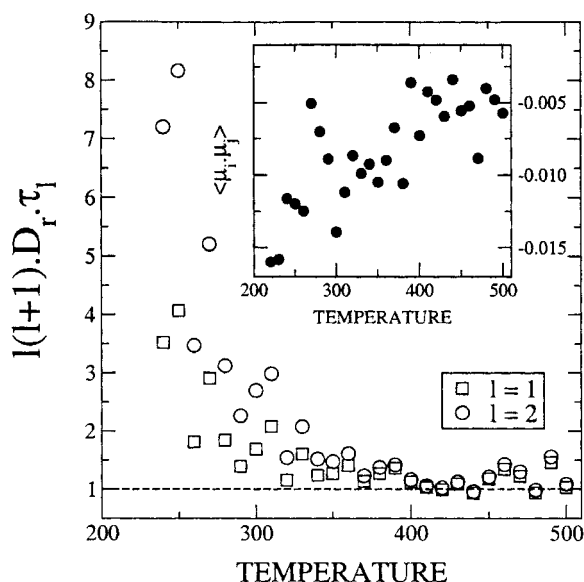


Figure 8. Temperature dependence of $l(l+1)D_r \cdot \tau_l$ where D_r is the rotational diffusion constant and τ_l are the correlation times defined as the time it takes for their respective time correlation functions $C_l(t)$ to decay e^{-1} of their initial values. $l(l+1)D_r \cdot \tau_l \simeq 1$ is expected for uncorrelated small angular steps dipolar motions (dashed line). The τ_l correlation times are given in [23, 36]. The average first neighbours two-molecule orientational correlations $\langle \vec{\mu}_i \cdot \vec{\mu}_j \rangle$ as function of temperature is given in the inset.

Low-frequency vibrational density of states ($\omega < 140 \text{ cm}^{-1}$) have been calculated and are shown in figure 9. Owing to the simplicity of our model, the internal vibrational contributions of the Cla molecule and the fast uniaxial rotations can not be reproduced. Clearly, the density of states exhibits two broad bands in good agreement with experiment. They can be seen both in the translational and the rotational contribution at 30 and 60 cm^{-1} at $T = 220$ K which indicates the presence of translation-rotation (R-T) coupling expected for orientationally disordered crystals. At higher temperature, R-T coupling decreases strongly which allows us to separate clearly translational and orientational contribution of the density of states. The change of the lineshape of the density of states bands has been studied following the experimental fitting procedure. The characteristic frequencies of both bands have been obtained from the translational density of states and are displayed in figure 10. As observed experimentally, a change of the evolution as function of the temperature is clearly seen at T_x .

The presence of local order as proposed in [25] and by the present Raman investigation has been searched in the MD simulation data. We have calculated the average first neighbours two-molecule orientational correlations $\langle \vec{\mu}_i \cdot \vec{\mu}_j \rangle$ where $\vec{\mu}_i$ is the individual dipole vector. Clearly, we have found a slightly negative value for $\langle \vec{\mu}_i \cdot \vec{\mu}_j \rangle$ which indicates a weak antiferroelectric order increasing continuously when lowering the temperature (see inset in figure 8). However, no clear anomaly was detected at T_x .

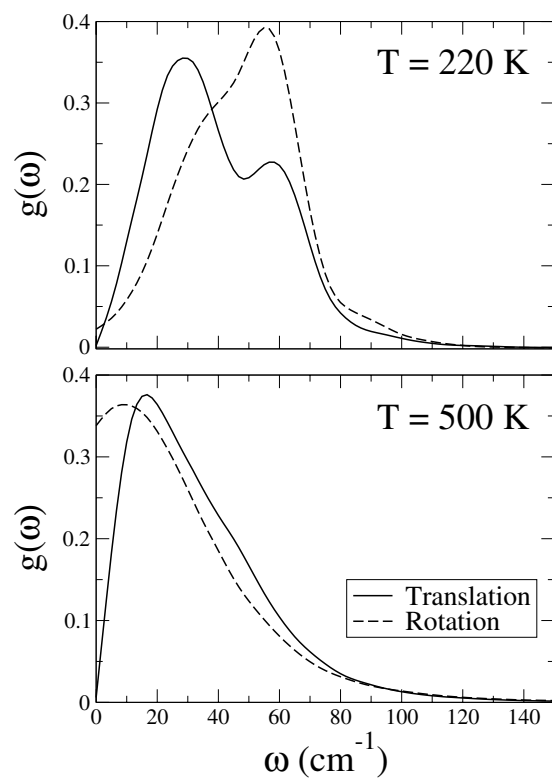


Figure 9. Translational (solid line) and rotational (dashed line) normalized density of states as function of the frequency at $T = 220$ and 500 K. Data have been smoothed for clarity.

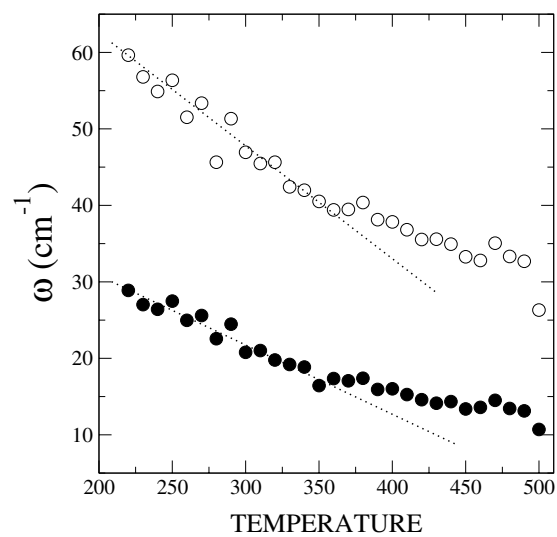


Figure 10. Temperature dependence of the frequency of the gaussian (full circle) and lognormal (open circle) components observed for the translational density of states. The dotted line is a guide for the eye.

5. Conclusions

For the first time, Raman scattering experiment and MD simulation investigations reveal that vibrational dynamics of orientationally disorder crystal Cla exhibit a crossover at the temperature T_x which is associated to the onset of slow dynamics i.e. non-exponential relaxations. It also shows that the change in the nature of the dynamics is closely associated to a local orientational ordering which can be nicely probed from the so-called bending mode of the Cla molecule. It should be noted that the bending-mode is clearly defined, well separated from the low-frequency contributions and exhibits a more pronounced changeover at T_x . Therefore, it can be considered as a very sensitive probe of the orientational dynamics in the substituted adamantane family. Furthermore, this work is perfectly consistent with previous calorimetric [25], NMR and MD studies [23, 24] performed on the same compound and very much in keeping with recent views proposed for a model glass forming liquid [19–21]. Our results obtained for Cla call for experimental and numerical studies of other glassy crystals.

Acknowledgments

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