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Temperature dependence of internal bandwidths in plastic adamantane by Raman light scattering

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Résumé. — La phase à désordre d'orientation de l'adamantane (208 K-541 K) a été étudiée par diffusion Raman de 209 K à 500 K. La bande de vibration à $1\,220\text{ cm}^{-1}$ de symétrie E a été enregistrée avec les symétries E_g et F_{2g} . Les spectres E_g , dus aux molécules ordonnées, sont élargis par un effet de temps de résidence. Les spectres F_{2g} , correspondant aux molécules en cours de réorientation, pourraient être attribués à la modification de la vibration interne par l'environnement pendant la rotation.

Abstract. — The ODIC phase of adamantane (208 K-541 K) was studied by Raman light scattering between 209 K and 500 K. The $1\,220\text{ cm}^{-1}$, E symmetry, vibrational line was recorded with E_g and F_{2g} symmetries. The E_g spectra, due to ordered molecules, are broadened by a residence time effect. The F_{2g} spectra, which correspond to molecules as they rotate, could be attributed to the modification of the internal vibration by the environment during the molecular reorientations.

1. Introduction.

We study here adamantane ($C_{10}H_{16}$) in a state usually referred to as plastic or ODIC (*Oriental Disorder In Crystals*), that is, in a situation in which the centres of mass of the molecules form a lattice (FCC in the case of adamantane) but the molecules display orientational disorder and undergo frequent reorientations. In this state, the tetrahedric adamantane molecule tends to rest in its cubic lattice in such a way that its three and fourfold symmetry axes are parallel to the three and fourfold axes respectively, of the crystal [1]. Neutron scattering experiments [2] show :

- 1) that the molecules undergo mostly 90° reorientations around their fourfold axes ;
- 2) that, even in the relatively small range of temperatures at which the experiments were performed, the residence time between reorientations decreases rapidly.

Positron annihilation experiments [3] between room temperature and the melting point show a drastic increase of the concentration of vacancies in the crystal (which are partly linked to the reorientations of the molecules).

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One could then expect an important variation with temperature of the rotational contributions to Raman spectra. We describe in this paper such an experiment performed on the $1\,220\text{ cm}^{-1}$ internal mode of adamantane, with molecular E symmetry.

2. Experiments.

Several technical problems have to be solved in order to be able to perform the experiments. The vapour pressure of adamantane is fairly high (0.1 mmHg at room temperature, 1.8 atm at 225 °C [4]) with the following consequences :

a) in a light scattering experiment, the incident beam tends to ruin the surface of the sample by a local heating which causes a transport process similar in principle to that used in vapour growth techniques [5, 6] ;

b) as the temperature increases, the sublimation process becomes so rapid that the sample simply disappears before the experiment is completed.

Problem *a)* had already been partially solved in a room temperature Brillouin scattering experiment [1] by keeping the sample in water. By doing this, one

— reduces the surface effects by index matching

— substitutes a transport in solution to the vapour transport. This is an improvement only if the solubility is small.

Consequently alcohol was substituted to water between -64 and 25 °C , glycerol between 25 and 75 °C and polyethyleneglycol 2000 (PEG 2000) between 75 and 225 °C [7]. We checked that the results did not depend on the liquid at temperatures at which two different liquids could be used.

Problem *b)* still remained as the liquid does not prevent the formation of bubbles of vapour. This was taken care of by enclosing the sample and liquid in an airtight pyrex cell, which in turn is set on a sample holder especially designed to resist the pressure.

The $1\,220\text{ cm}^{-1}$ [8] line was recorded between 209 K and 498 K (-64 °C and 225 °C). Both crystal E_g and F_{2g} symmetries [9] were used.

3. Results and treatment.

Typical spectra are shown on figure 1. At this stage, they have already been subjected to a digital filter which reduces markedly the noise without altering the bandwidth as has been checked by using various steplengths.

The E_g spectra are narrow and fairly intense and sided by two other lines at $1\,195$ and $1\,240\text{ cm}^{-1}$, the origin of which is unknown at present, although they would seem to persist in the low temperature ordered phase [10]. A Lorentz function was fitted to the central line. The resulting half widths at half maximum ⁽¹⁾ are shown on figure 2.

The F_{2g} spectra are broader and less intense (from 2 to 5 % of the E_g spectra), but their most interesting feature is their asymmetry which made their fitting by a single Lorentzian impossible. On the contrary, they could be resolved, by a two Lorentzian fit, into two contributions which had neither the same frequency nor the same width. Two remarks were then made :

— at each temperature, the narrower contribution had approximately the same frequency and width as the corresponding E_g spectrum ;

— the intensity ratio between the narrow and broad contributions was mainly sample dependent.

⁽¹⁾ The elastic scattering peak was recorded ($\text{HWHM} \approx 0.6\text{ cm}^{-1}$) and introduced in the fit by convolution with the Lorentz function in order to account for the broadening by the spectrometer. Consequently the computed HWHMs do not have to be corrected for instrumental effects.

Fig. 1. — Typical room temperature spectra of the E molecular symmetry line at 1220 cm^{-1} . a) E_g symmetry relative to the crystal; b) F_{2g} symmetry relative to the crystal. The arrow points to the effective F_{2g} rotational peak. Intensity units are arbitrary and unrelated between a) and b).

Fig. 2. — HWHM of the E_g spectra versus temperature. Full circles refer to the VV spectra [9] and crosses to the HH spectra. The difference between them gives a measure of accuracy. Open circles refer to neutron scattering results [2].

It was thus concluded that the narrow contribution was simply an optical leak of the E_g spectrum, while the broad one was the actual F_{2g} spectrum. Another two Lorentzian fit was then performed with the width of the narrow Lorentz function set at the value given by the E_g spectrum.

This practically did not alter the quality of the agreement between a recorded spectrum and a computed one and an example is given on figure 3. The resulting F_{2g} HWHM and distance between the E_g and F_{2g} peaks [11] are shown on figure 4.

Fig. 3. — Experimental F_{2g} spectrum (dots) and the two Lorentzian fit (full line) at 75 °C. The intensity unit is arbitrary. The distance between two points is 0.7 cm^{-1} . Remnants of the two side bands noted in the E_g spectra are visible. The one Lorentzian fit of the E_g spectra is of a better quality.

Fig. 4. — HWHM of the F_{2g} spectra (lefthand scale; closed circles : HV ; crosses : VH) and distance between E_g and F_{2g} peaks (righthand scale; open circles : HV ; triangles : VH). The F_{2g} spectrum is very weak at temperatures below -50 °C . At $T = -64 \text{ °C}$ it could not be measured with VH polarization. The lines are only guides for the eye.

4. Discussion.

4.1. — The results presented in section 3 are somewhat unusual as the HWHM are quite different in the two symmetries, for one thing and the peaks do not coincide for another. Such a situation has not been reported up to now except at one temperature in the case of cyano-adamantane [12].

Although it is not the purpose of this letter to provide a thorough interpretation of the results, we shall offer a tentative explanation of them.

As pointed out in part I, the adamantane molecule rests most of the time in one of two equiprobable equilibrium positions so that its three fourfold axes are parallel to the fourfold axes of the crystal. The projection of the molecular Raman tensor on the crystal axes is then purely diagonal, so that, in this configuration, the E vibration contributes only to the E_g spectrum. Therefore the F_{2g} spectrum results from the short time when the molecule is reorienting and the above symmetry rule does not apply.

4.2. — As the E_g spectra relate to immobile molecules, the rotational contribution to their bandwidth can be attributed only to a residence time effect : as long as a molecule rests at the bottom of its potential well, it vibrates with frequency ω_0 . During a reorientation, this molecule feels a different environment, as it must overcome a potential barrier, and thus vibrates with frequency $\omega_0 + \delta\omega(\Omega)$. When it reaches another equivalent potential well, it resumes its vibration with frequency ω_0 . This appears as an interruption of the vibration ω_0 by reorientations [13].

This effect alone is, however, unable to explain the measured bandwidth (for which the errors are certainly less than 0.5 cm^{-1}) and its thermal evolution : if one extrapolates the lifetimes measured by neutron scattering at 301 K and 373 K [2], to the whole temperature range of our experiments, one finds that the contribution of the residence time effect to the Raman width is negligible at 209 K and amounts only to 2 cm^{-1} at 498 K (Fig. 2). The additional width can be due to many causes, among which we can point out the following three :

- the coupling between two neighbouring molecules vibrating at the same frequency can affect the frequency of a molecule at rest when the second is rotating. This would act as a dephasing lifetime and cause an apparent decrease of the lifetime by a factor up to 12, depending on the efficiency of this coupling ;

- the orientational disorder of the neighbouring molecules can cause an inhomogeneous broadening by shifting slightly the vibrational frequency of the individual molecules at rest ;

- the vibrational lifetime of the mode is non infinite, due to intra- and intermolecular anharmonicities.

4.3. — As shown in section 4.1, the F_{2g} spectra of the E line relate to a reorientating molecule. In a theory in which the rotational broadening is a consequence of the rotation of the dielectric tensor attached to a vibrating molecule [14, 15], one expects :

- a) the peaks in both polarizations to have the same frequency ;

- b) in the case of a $2\pi/n$ reorientation related to free rotations, the bandwidth to be roughly equal to $\frac{n}{(2\pi)^2} \sqrt{\frac{kT}{I}}$ and thus to vary approximately as $\sqrt{T}$.

Neither condition (a), as shown in 4.2, nor (b) (Table I) is fulfilled.

The existence of a possible frequency shift has already been accounted for in section 4.2 when it was explained that, as a molecule reorients, it feels a different environment and thus vibrates at another frequency. We suggest that the observed width is caused by a dynamical inhomogeneous broadening effect. Inhomogeneous broadening usually results from the fact that the molecules feel a variety of environments due to the disorder, and vibrate with a distribution of frequencies [16]. In our case, it is a dynamical effect as it is caused by the rotation of the molecule itself : as a molecule rotates it overcomes a potential barrier and its internal vibration is thus continuously altered as it rotates. This alteration depends on the height of the potential barrier, and with increasing temperature, higher and higher barriers can be overcome leading to more and more important alterations of the vibrational frequency. Such effects could explain

Table I.

T	$\frac{4}{(2\pi)^2} \sqrt{\frac{kT}{I}}$	WHM	WHM	$\frac{\text{WHM}}{\sqrt{T}}$	$\frac{\text{WHM}}{\sqrt{T}}$
K	cm^{-1}	HV cm^{-1}	VH cm^{-1}	HV $\text{cm}^{-1} \text{K}^{-1/2}$	VH $\text{cm}^{-1} \text{K}^{-1/2}$
209	0.34	very weak			
218	0.35	6.8	8.4	0.46	0.57
248	0.37	7.1	7.1	0.45	0.45
298	0.41	6.9	6.9	0.40	0.40
348	0.44	7.9	8.1	0.42	0.43
398	0.47	9.5	9.4	0.48	0.47
448	0.50	12.5	12.4	0.59	0.59
473	0.52	12.2	12.1	0.56	0.56
498	0.53	13.0	13.0	0.58	0.58

Column 2 : expected bandwidth in a classical 90° rotational model calculated with $I = 7.11 \times 10^{-45} \text{ kg m}^2$.

Columns 3 and 4 : measured bandwidths.

Columns 5 and 6 : bandwidths divided by $\sqrt{T}$ showing that they are not proportional whatever rotation angle is chosen.

both the width of the F_{2g} spectra and its important increase with temperature ⁽²⁾. The slow variation with temperature of the frequency difference between the E_g and F_{2g} maxima has in such a case no straightforward explanation. The experimental results suggest that the thermal expansion which decreases the intermolecular interactions could explain this effect but this is by no means the only possibility.

More discussion is certainly needed, but we believe our results show important effects caused by the combination of rotations and temperature.

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- [7] PEG 2000 is solid at room temperature. Other compounds have been tried but the solubility of adamantane at high temperature is not an easy problem. Glycerol was a good candidate, but it creates a background in the spectra, which becomes both intense and fluctuating around 150 °C and the signal to noise ratio consequently decreases dramatically.
- [8] Absolute frequencies are not given in this paper with any degree of accuracy as it was not the purpose of the experiment. On the contrary, frequency shifts are accurate to the precision of the fit.

⁽²⁾ Such a contribution should also be present in the E_g spectrum. An order of magnitude calculation based on the lifetime of the molecule in its potential well shows that this contribution is too weak to be detected under the intense normal E_g spectrum.

- [9] The adamantane single crystal (grown by a sublimation method and checked through Laue X ray tests) was set with a fourfold axis vertical and two perpendicular twofold axes parallel to the incident beam and observation direction resp. Four different combinations can be used : 1) the incident beam is polarized vertically and analysis of the scattered light is also vertical (VV) providing an $A_{1g} + 4 E_g$ spectrum ; 2) vertical polarization and horizontal analysis (VH) : F_{2g} spectrum ; 3) HV : F_{2g} ; 4) HH : $3 E_g$. The depolarization ratio measured on the 758 cm^{-1} , A line in VV and VH situations is inferior to 2 %.
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