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Raman study of structural relaxation and boson peak in amorphous films of adamantane

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Dedicated to Prof. James R. Durig

Abstract

Low-frequency Raman scattering was used to study amorphous solid films of adamantane, a globular non-polar hydrocarbon molecule. As evidenced by its spectral characteristics this type of disorder is different from the orientational disorder found in the room temperature plastic phase by the absence of the translational order as well. This gives rise to the boson peak related to acoustic phonons which gradually disappears upon heating with simultaneous emerging of the phonon line at $50\,\mathrm{cm}^{-1}$ which characterizes the low-temperature ordered phase of adamantane. Adamantane dynamics resembles that of C_{60} fullerene although not in the same temperature range. All this makes adamantane an attractive system that could serve as a practical reference in molecular simulation studies of the glassy phase of model fluids.
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1. Introduction

The study of amorphous solids or glasses (obtained when a viscous super-cooled liquid passes on cooling into the amorphous solid phase) is still a challenging subject of interest from a scientific and technological point of view (see, for example [1]). Another way to produce an amorphous solid of almost any substance is by fast enough cooling. One way to achieve such a cooling rate is deposition of gas molecules onto a cold metal substrate. The extreme rate of temperature decreasing causes formation of highly disordered molecular deposits. In recent years, the controlled deposition of hydrocarbon thin films (various types of amorphous carbon, diamond and polymeric structures) is the subject of the intense investigation [2]. The study of amorphous molecular film is important not only for basic knowledge of molecular interactions, but also because of their potential of being used in technology.

The disorder in amorphous systems as obtained by either way described above has a strong effect on low-energy vibrational dynamics and consequently the low-frequency Raman scattering is used to study the structure of amorphous films. In the low-frequency Raman spectra of disordered materials three contributions can be discerned [1]: (i) a boson peak (BP) due to acoustic vibrational excitations of any wavevector with an intensity maximum between 10–$70\,\mathrm{cm}^{-1}$, (ii) a quasi-elastic (QE) scattering band centred around zero frequency and for $\tilde{\nu} < 20\,\mathrm{cm}^{-1}$ that overlaps with BP and is due probably to relaxational motions [3,4] and (iii) a vibrational contribution due to optical phonons. The physical origin of the BP has been the subject of numerous studies and most likely it is the consequence of static disorder. The lack of periodicity causes the selection rule $\vec{q} = 0$ to break down and all the vibrational modes become Raman and IR active [5]. Martin and Brenig [6] have described this phenomenon as a wide background of Brillouin scattering by an amorphous solid. According to their model the density of states of acoustic phonons and the Gaussian structural correlation function give rise to the BP. The comparison with inelastic neutron

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scattering data [7] indicated that BP is connected to the excess in the vibrational density of state revealed by the specific heat measurements [8].

The annealing processes in amorphous films of naphthalene and anthracene [9], and biphenyl and toluene [10] have showed the characteristic structural relaxation, which eventually lead to the crystalline structure. A hypothesis has also been put forward [10] that the low-frequency Raman bands ($<150 \, cm^{-1}$) in liquids and amorphous organic solids may rather be connected to optical phonons associated with librational motions of molecules or low-frequency skeletal vibrations of flexible molecules (further examples of such molecules also capable of forming glass phase are *ortho*-terphenyl [11] and benzophenone [12]). *ortho*-Terphenyl and benzophenone exhibit BPs with maximum at around $20 \, cm^{-1}$ which is also found, as shown below, in the amorphous adamantane. Since to a very good approximation adamantane molecules can be considered rigid (the lowest molecular vibration is a carbon skeleton deformation at $402 \, cm^{-1}$ [13]), analogously to C_{60} fullerene molecules [14], optical phonons contributing to the BP, if any, could only be due to the librational molecular motions.

The study of Raman scattering from intramolecular and intermolecular modes in adamantane films was thus performed to obtain information regarding film structure. Structural characteristics of the adamantane film and the nature of the intermolecular forces are estimated not only from the intensity and spectral shape but also from the depolarisation ratio of the recorded Raman spectra. The plastic phase of adamantane is orientationally disordered (the plastic phase possesses the long-range translational order while the correlation exists only between librational motions of first neighbours). A model in which adamantane molecules reorient by $90°$ jumps around the crystal C_4 axis with the reorientation correlation time of 20 ps at room temperature has been shown to be consistent with incoherent quasi-elastic neutron scattering and NMR relaxation time measurements [15]. The nature of disorder in adamantane film as shown below by comparison between the low-frequency spectra of the two adamantane phases is quite different. Adamantane is thus a system exhibiting different types of disorder. Since its orientationally disordered and fully ordered phases have been thoroughly investigated, the amorphous phase will be discussed in relation to them. We show how small and rigid non-polar molecules interacting only via van der Waals forces easily make amorphous state and manifest relaxational behaviour.

2. Experimental

Thin films of adamantane were prepared by evaporation and deposition of the sample onto a cold metal substrate whose surface was coated with gold. The low-temperature environment was produced by a closed cycle helium cryostat CTI Cryogenics (Model 21). The metal substrate was mounted on a cold finger of the cryostat using indium as a conducting junction. While the substrate was cooled to the deposition temperature, the sample was contained in a glass ampoule cooled with liquid nitrogen (at 77 K adamantane molecules move around at $0.07 \, km \, s^{-1}$, i.e. the impact velocity was well below the breaking up limit of $15 \, km \, s^{-1}$ [2]). The deposition temperature was always 10 K, i.e. we have not investigated the film formation as a function of substrate temperature. The base pressure in the vacuum chamber was about $10^{-4} \, Pa$. Films were deposited by the evaporation for few minutes. The film thickness could not be measured but certainly was great enough so that any interference effect due to the reflection of the light on the metal substrate could have been ignored. The film was kept at least a half-an-hour at a given temperature before recording a spectrum at the $90°$ geometry. The recording lasted at least one hour with a subsequent check for any intensity change during recording. The adamantane films were annealed through several slow cycles between 10 and 180 K, i.e. below the phase transition temperature (208 K).

The Raman spectra of adamantane films were recorded from 3000 to $10 \, cm^{-1}$ on a Dilor Model Z24 spectrometer using 514.5 nm argon ion laser excitation. Scattering geometries, polarized (VV) and depolarized (VH), were employed. The laser power was kept below 100 mW at the sample surface. The slit width was 300 μm corresponding to the spectral slit width of $2.88 \, cm^{-1}$.

3. Results and discussion

The adamantane molecule is a rigid hydrocarbon ($C_{10}H_{16}$) with a tetrahedral symmetry of the point group T_d. Its normal vibrations span the representation $5A_1 + A_2 + 6E + 7F_1 + 11F_2$, where A_1 ($\nu_1-\nu_5$), E ($\nu_7-\nu_{12}$) and F_2 ($\nu_{20}-\nu_{30}$) are Raman active vibrations and only the F_2 vibrations are IR active. The A_2 (ν_6) and F_1 ($\nu_{13}-\nu_{19}$) vibrations are forbidden both in Raman and IR spectra. The space group of the high-temperature orientationally disordered phase is $Fm\bar{3}m$ (O_h^5). There are four molecules in the unit cell each being a superposition of the two equally probable orientations. In order to proceed further with the vibrational analysis we assume that the high-temperature phase is built from the perfect octahedral rigid molecules at sites with O_h symmetry. Thus, the molecular site symmetry is not lower than that of the free molecule, and the selection rules are not expected to change and no splitting of vibrational bands is predicted for this phase. On the other hand, in the low-temperature ordered phase (tetragonal space group $P\bar{4}2_1c$ (D_{2d}^4)) the site (S_4) and factor group symmetry (D_{2d}) are lower than that of the free molecule and new selection rules are effective. The normal modes of the molecule in the ordered phase are now distributed among symmetry species of D_{2d} according to $11A_1 + 7A_2 + 7B_1 + 11B_2 + 18E$. Vibrations in the A_1, B_1, B_2 and E classes are Raman active, i.e. the forbidden A_2 and F_1 vibrations of T_d becomes Raman active in the ordered phase. Thus, the degenerate normal modes of a