

EXCITATIONS IN THE COMMENSURATE PHASE OF H₂, D₂ AND HD ON GRAPHITE

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We measured the excitations of the hydrogen isotopes (H₂, HD, D₂) adsorbed on graphite in the commensurate phase. A simple model of two in-plane springs reproduces well the observed neutron spectra and gives the dispersion relations. The isotopic mass effect alone cannot explain the energy shift of these modes.

The behaviour of the quantum gases hydrogen (H₂) and its isotopes, deuterium (D₂) and deuterated hydrogen (HD), is of considerable experimental and theoretical interest, in particular for the study of their phase transitions in two dimensions (2D). These gases adsorbed on graphite are a good approach to an ideal 2D system in the incommensurate phase, but lock at lower coverages into a ($\sqrt{3} \times \sqrt{3}$) R30° commensurate phase (C-phase) due to the graphite surface potential corrugation. The structure of the different phases has been investigated mainly by neutron scattering [1, 2]. The C-phase presents a nearest neighbour distance (a_{nn}) of 4.26 Å, even though a_{nn} in the hcp-plane for the 3D solid hydrogen is nearly 20% smaller [3]. It is the high compressibility due to zero point motion of the adsorbed molecules that makes this structure energetically favourable [4]. To understand the influence of the substrate on the different phases of the adsorbate it is necessary to know the substrate–adsorbate and adsorbate–adsorbate interactions. Here we report inelastic neutron scattering (INS) measurements in the commensurate phase: the dependence of the excitations on the different isotopes.

The out-of-plane oscillation of the adsorbed molecules is given by the variation of the adsorption potential in the direction normal to the graphite surface plane. The in-plane oscillations in the C-phase are given mainly by the corrugation of this potential along the surface. In this work only the in-plane oscillations will be presented. In earlier INS experiments [1, 5] only a

dispersionless excitation could be seen and the interpretation was that the molecules oscillate in the wells produced by the substrate as independent oscillators. In recent measurements [6] of D₂ on graphite realized with a higher energy resolution we were able to measure the coupling between the D₂ molecules in the C-phase. First principle calculations [7] have been realized as well on these systems. We add here high resolution measurements for HD and H₂ on graphite and compare them to the mentioned calculations and to the D₂ results.

The INS data were taken with the three axis spectrometer IN3 at the ILL with a fixed final energy ($E_F = 0.99$ THz), a Be filter after the sample and a horizontally focusing analyzer. The energy resolution across the elastic line was 0.033 THz (1.59 K) FWHM for D₂ and HD, and 0.049 THz (2.36 K) for H₂. The sample cell was filled with papyex sheets, the graphite basal plane being in the neutron scattering plane. This geometry favours the measurement of the in-plane excitation.

The INS spectra for D₂, HD and H₂ (fig. 1) were taken at a coverage of a completely filled monolayer in the C-phase at 4 K. This coverage consisted of 315 cc STP of gas. In all cases the scattering from the sample without adsorbed gas was subtracted as background. The solid line in the figure is the fit as described below.

To analyze these systems we used a simple Born–von Karman model: nearest neighbours were connected by central springs on a triangular grid and each adsorbed molecule was also at-

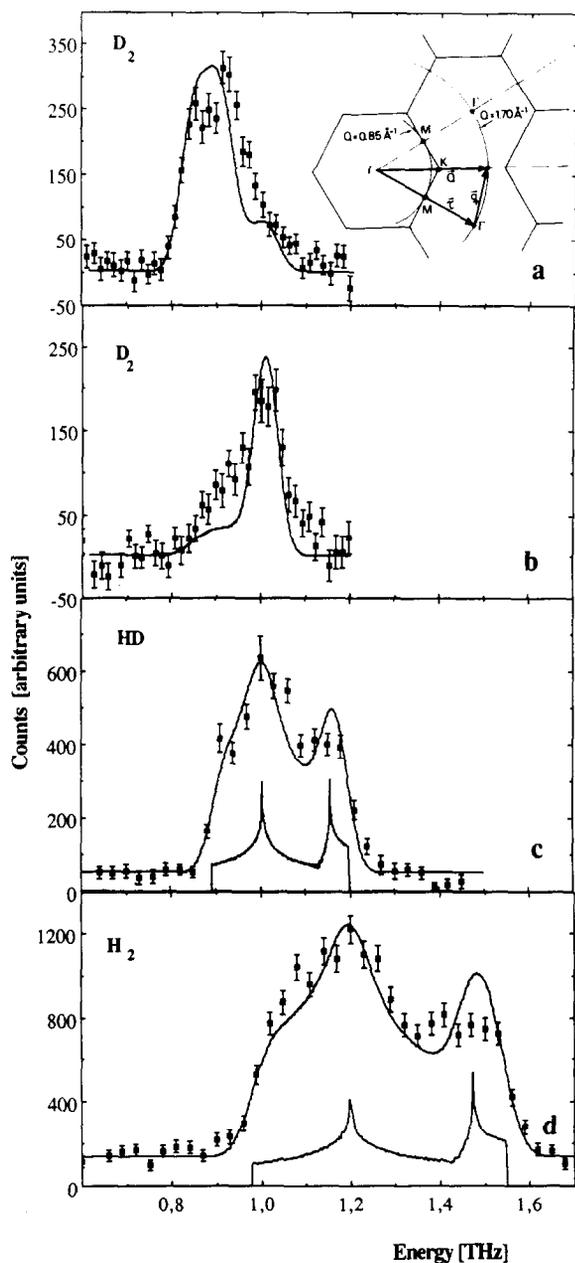


Fig. 1. Neutron inelastic data of the hydrogen isotopes adsorbed on graphite in the commensurate phase (the background has already been subtracted). At the top are the deuterium (D_2) spectra for $Q = 1.70 \text{ \AA}^{-1}$ (a) and $Q = 0.85 \text{ \AA}^{-1}$ (b), the full line is the fit to the data as explained in the text and in ref. [6]. The inset shows the region of reciprocal space covered by these two scans. One example of a scattering triangle is sketched: it corresponds to the excitation of a transverse zone boundary phonon (Q is the total momentum transfer: τ is a reciprocal lattice vector and q is

tached by another spring to the substrate at its commensurate position (both are in-plane springs) [6]. No coupling between this structure and the phonons of the substrate was taken into account. For D_2 which has a mainly coherent cross section the adequate choice of momentum transfer Q can be used to distinguish different phonon polarizations. The measured signal consists of a directional average over all phonons for which the scattering triangle closes [6, 8]. This is depicted in the inset of fig. 1a (circles for $Q = 0.85 \text{ \AA}^{-1}$ and 1.70 \AA^{-1}). Those phonons for which a singularity in the density of states (DOS) exists along the path in reciprocal space contribute most to the signal. The scan at a momentum transfer $Q = 1.70 \text{ \AA}^{-1}$ focuses on the phonons at the zone center and the transverse phonons at the zone boundary. The scan taken at $Q = 0.85 \text{ \AA}^{-1}$ (fig. 1b) focuses on the longitudinal zone boundary phonon. The solid lines in figs. 1a and 1b are the calculated lineshapes for the two Q values based on the dispersion relation deduced from the Born-von Karman model, taking into account the molecular form factor, the one phonon coherent and incoherent dynamic structure factors, the 2D powder averaging, the mosaic spread of the sample around the c -axis and the resolution ellipsoid of the spectrometer [6]. H_2 and HD are mainly incoherent scatterers (for H_2 this is only true in the first hours of the experiment due to the conversion to the para-state). This implies that the INS spectra reflect the phonon DOS. In figs. 1c and 1d the solid lines are given by the DOS also calculated with the Born-von Karman model convoluted with the energy resolution of the instrument. A flat background has been included in the fits.

The parameters which characterize the dynamics of the three isotopes in the C-phase are given in table I together with the theoretical

the phonon momentum). The deuterated hydrogen (HD) and the hydrogen (H_2) spectra taken at $Q = 1.70 \text{ \AA}^{-1}$ are shown in parts (c) and (d), respectively. The curve through the experimental points is the fit with the phonon density of states of our model convoluted with the energy resolution of the spectrometer. The unconvoluted density of states is drawn beneath it.

Table I

Parameters obtained from the fits characterizing the density of state for the in-plane modes of the $(\sqrt{3} \times \sqrt{3})$ R30° commensurate phase of the hydrogen isotopes adsorbed on graphite (in parenthesis the theoretical values of A. Novaco [7] and between brackets the frequencies for the Einstein-mode obtained with the classical adsorption potential of ref. (9)). Indicated are the following: Z.c. gap is the zone center gap energy, Width is the DOS width, Tran. peak and Long peak are the peaks arising from the transverse and longitudinal phonons in the DOS, respectively (all values are in kelvin). The uncertainty in the experimental values is estimated to be ~ 2 K.

	H ₂	HD	D ₂
Z.c. gap	47.3 (46.6) [49.7]	43.2 [40.5]	40.0 (36.9) [35.2]
Width	27.5 (42.1)	14.7	9.5 (14.8)
Tran. peak	57.9 (64.9)	48.8	43.3* (44.2)
Long. peak	71.4 (83.8)	55.8	48.1 (50.3)

* The experimental data of fig. 1a suggest a value of 44.4 K for the transverse peak.

values of A. Novaco [7]. A good overall agreement between experiment and theory is found and the DOS shows the expected trend for the different isotopes. Unfortunately there are not yet calculations for HD available. The gap, which reflects the corrugation of the substrate, is found at a somewhat higher energy for both species, but the agreement is very reasonable. A significant point is that the width of the DOS is overestimated in the calculations (the theoretical values are $\sim 50\%$ too high for H₂ and D₂). This implies that the interaction between the adsorbed molecules is in fact weaker than expected. The values of the phonon gap and the width of the DOS do not scale with the inverse of the square root of the mass of the isotopes as expected for a classical system. H₂ which has a larger zero point motion interacts more strongly with its neighbours than HD and D₂. This is evidenced by the width of the DOS which is for H₂

nearly three times that of D₂, instead of being $\sqrt{2}$ due to the isotope effect. At the same time the corrugation of the substrate is averaged out due to the zero point motion and thus the gap for H₂ lies much lower than what one would expect considering only the isotopic shift.

The present data show clearly that the excitations found in the commensurate phase of the hydrogen isotopes adsorbed on graphite are not only due to the corrugation of the substrate, but are also produced by the coupling to the neighbouring molecules. The mass dependence of their phonon density of states can only be interpreted taking into account the quantum character of these systems.

Acknowledgements

Special thanks are given to A. Novaco for many helpful communications. This work has been partially supported by the Federal Ministry of Research and Technique (BMFT) of Fed. Rep. Germany.

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