

ROTATIONAL EXCITATION AND OUT-OF-PLANE VIBRATION OF para-H₂ AND HD ADSORBED ON GRAPHITE

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Recently detailed inelastic neutron measurements[1] of the in-plane excitations of hydrogen isotopes (H₂, HD and D₂) adsorbed on graphite have been reported and good agreement with theoretical calculations[2] has been found. A basic assumption in these calculations is that the molecules are in the $J=0$ rotational ground state. To investigate the validity of this assumption a more detailed analysis of the quantum mechanical state of this system has been performed[3]. It showed that the lowest energy state has a 0.999 $J=0$ component indeed, confirming the previous hypothesis. As an additional feature, the calculations predict a splitting of the first excited state into a doublet formed by the $M_J=0$ and $M_J=\pm 1$ states. This splitting is due to the anisotropy of the adsorption potential and thus the molecule feels a different interaction when the axis of rotation, classically speaking, is perpendicular or parallel to the adsorption plane. However, the magnitude of this effect as measured by NMR measurements[4] is an order of magnitude smaller than the theoretical prediction. This suggests that the treatment of the coupling between rotational and translational modes must still be refined.

We have performed neutron inelastic scattering measurements in order to observe the rotational transition of adsorbed H₂ and HD and also the out of plane vibration of these molecules. We used two types of substrate: a) a graphite powder[5] and b) oriented graphite foils[6]. The coherence length of these two substrates is 40Å and 300Å, respectively. The spectra taken before any gas was adsorbed were used as background and subtracted from the following runs. The measurements were carried out at the three axis spectrometer IN3 at the Institute Laue-Langevin. We used a fixed final energy of 0.98THz, both a Cu111 and a PG002 monochromator, a PG002 analyser and a Be filter positioned after the sample. The resolution obtained from the elastic line using a vanadium sample was 0.033THz (FWHM) for the PG002 monochromator. The FWHM calculated energy resolution at 3.5THz (the energy of the $J=0 \rightarrow 1$ transition for H₂) was 0.21THz and 0.12THz for the PG002 and the Cu111 monochromators, respectively. (1THz = 4.14meV = 48.28K)

Graphite Powder Substrate

The spectra taken with an adsorbed commensurate monolayer of H₂ present two peaks between 3 and 5.5THz (fig.1). The first one at an energy of 3.53THz is identified as the $J=0 \rightarrow 1$ rotational transition. Its value coincides very accurately with the one quoted in the literature for a free H₂ molecule[7] showing little influence of the presence of the substrate. The expected splitting of 0.64THz[3] is not detected, in agreement with the NMR data[4]. A spectrum taken at 0.5K did not show any difference to the one at 3.7K. The broader peak at 4.7THz can be assigned to the out-of-plane mode of the molecule vibrating against the substrate. The large width of this mode is due to its coupling to the phonons of the graphite substrate[8]. This mode disappears when the H₂ layer melts at 18K. The rotational transition peak, on the other hand, only loses intensity due to the increased Debye-Waller factor.

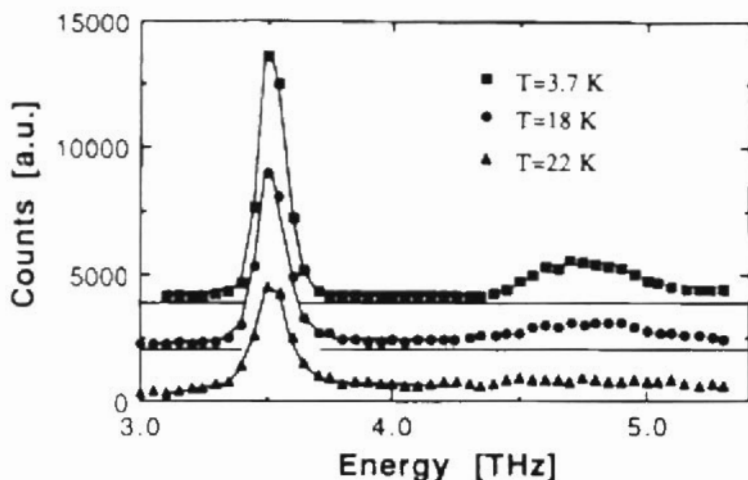


Figure 1. Spectra taken in the commensurate phase of H_2 adsorbed on graphite powder as a function of temperature ($Q=2.30 \text{ \AA}^{-1}$). The successive runs are displaced by 2000 counts.

Oriented graphite substrate

To be able to study the polarization of the above mentioned modes in more detail we used an oriented graphite[6] substrate. The graphite platelets were mounted with their c-axis in the scattering plane, thus allowing one to choose between Q transfer parallel and perpendicular to the adsorption plane (in the following called in-plane (IP) and out-of-plane (OP) polarizations, respectively).

Rotational transition

In the commensurate and full monolayers of H_2 , the rotational transition peak shows no difference at all between both polarizations and with respect to the powder substrate. A side peak appears at 3.41 THz (FWHM = 0.09 THz) when increasing the coverage to a bilayer in the OP configuration. No change is seen in the IP spectra. The origin of this second peak is not clear: it could be due either to a vibrational excitation of the double layer or to a splitting of the rotational transition. The second possibility seems unlikely, since this side peak shows up as an extra intensity when comparing the two polarizations, but a more detailed study should be performed.

The rotational transition for HD is found at 2.68 THz, very close to the free molecule value[7]. No splitting could be observed within the experimental resolution (FWHM = 0.21 THz, predicted splitting 0.64 THz). Furthermore, the transition energy does not depend on coverage up to the full monolayer.

Out-of-plane vibration

Similar to the graphite powder substrate, the OP vibration shows up for both gases, H_2 and HD, as a broad feature, due to the coupling to the graphite surface modes. For H_2 , the OP mode again appears at 4.7 THz, whereas for HD it is found at 3.6 THz due to the higher molecular mass. In contrast to expectation little change in intensity is observed between IP and OP configurations, indicating that this mode does not have a well defined polarization. Increasing the coverage to a full monolayer affects this mode strongly: the define peak disappears, and only a diffuse intensity distribution

remains (fig.2). In the bilayer a peak reappears at 4.7THz and a second one seems to show up at 5.5THz. This second mode may be due to an optic like interlayer vibration.

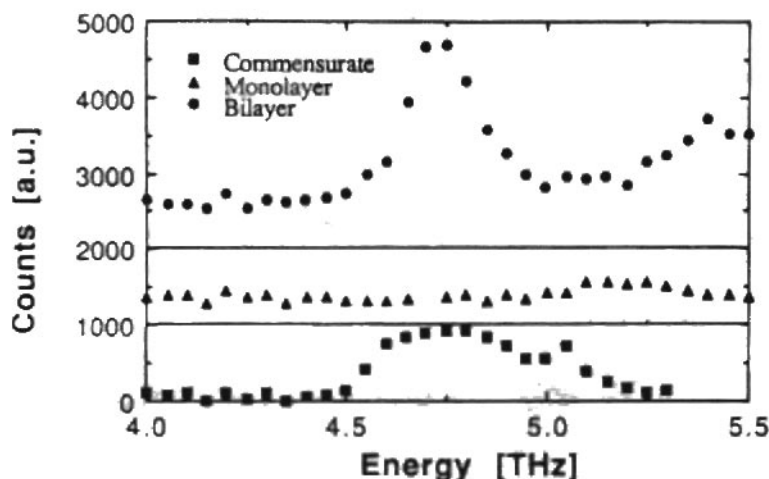


Figure2: Spectra of H_2 adsorbed on Papyex as a function of coverage ($T=4K$, $Q=2.30\text{\AA}^{-1}$). The successive runs are displaced by 1000 counts.

In summary, we have investigated two high-frequency excitations in H_2 and HD adsorbed on graphite: i) The $J=0 \rightarrow 1$ rotational transition, for which no splitting could be observed within the experimental resolution, indicating that the effect discussed in ref. 3 must be at least a factor of five smaller than predicted; ii) The out of plane mode, whose frequency at 4.7THz and 3.6THz for H_2 and HD, respectively, agrees well with the one obtained using Steele's adsorption potential.

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