INELASTIC NEUTRON SCATTERING STUDY OF THE VIBRATIONAL PROPERTIES OF C_{60}

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Solid C_{60} is a prototypical example of a molecular solid with very strong *intra*molecular and very weak *inter*molecular bonds. The high symmetry of the C_{60} molecule is certainly a major reason that it has attracted considerable interest. Moreover, it also greatly facilitates theoretical computations of its properties, and so C_{60} has become the best studied member of the fullerene family. For this reason, C_{60} can be considered as an ideal testing ground of theories for strong (covalent) forces as well for weak (van der Waals-like) forces. The most detailed information for a check of the theoretical predictions can be obtained by inelastic neutron scattering, and so we have undertaken a series of experiments to explore the vibrational properties of C_{60}. In the beginning, only the external vibrations could be studied because of the small size of the available single crystals (V~5 mm³)[1,2]. With the advent of fairly large single crystals (V~100 mm³) we were able to investigate the internal vibrations, too, with energies up to E=70 meV. Moreover, we were able to study the pressure dependence of the external vibrations. In the following, we summarize the results of the most recent experiments.

An isolated C_{60} molecule has 46 distinct vibrational modes. When the molecules are packed into a lattice, the intermolecular interactions give rise to mode splittings and to some dispersion. However, these effects are rather small due to the weakness of the intermolecular forces and can therefore be neglected . So, the problem of verifying the results of a certain theory reduces to verify the predicted *frequencies and displacement patterns* of the eigenmodes of the C_{60} molecule. We emphasize that a good agreement between calculated and experimental frequencies is of little value unless it has been checked that the observed mode has the same character as the calculated one. A minimum requirement is that the symmetry of the displacement pattern of the observed mode is the same as predicted for this frequency. However, as most symmetry classes contain more than one member, their displacement pattern is not determined by symmetry alone, but by the force field as well. This is demonstrated in Fig. 1, where we plotted the displacement patterns of a number of C_{60} eigenmodes, including those of the three lowest modes of H_g symmetry. Inelastic neutron scattering has the particular advantage that it allows one not only to unambiguously assign an observed frequency to a mode of a certain symmetry but, moreover, to check in detail whether the predicted displacement pattern

is correct or not. To this end, energy scans have to be made at many different points in reciprocal space. As can be seen from Fig. 2, the calculated scattering cross section versus momentum transfer differs widely for modes of the same symmetry but having different frequencies.
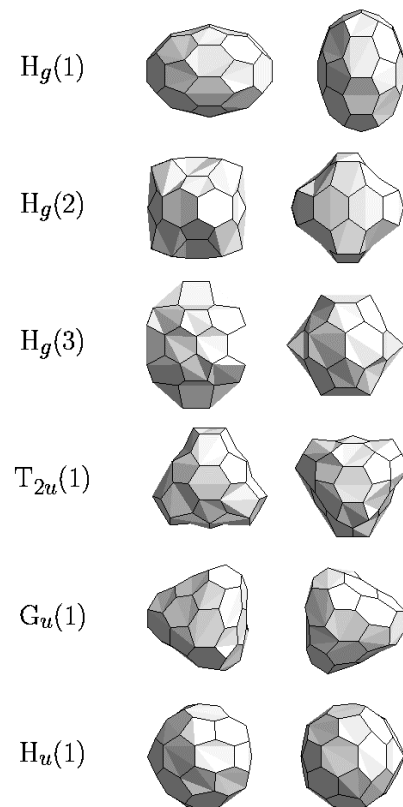

*Figure 1: Displacement patterns for five different eigenmodes of the C_{60} molecule. The elongations are strongly exaggerated for the sake of clarity. The left-hand and the right-hand figures correspond to extremal distortions following each other at time intervals 1/2 **n**. Eigenvectors are taken from the ab initio calculations of Bohnen et al. (Ref. 4).*

Our results revealed that several modes had been assigned incorrectly in the literature. Furthermore, we were able to show that *ab-initio* theory based on the local density approximation[4] describes not only the mode frequencies with high accuracy (~ 2%), but also the eigenvectors in a very satisfactory way. We note that the agreement between calculated and observed eigenvectors was significantly worse for a sophisticated model fitted to the experimental frequencies[5], which shows that a good agreement between calculated and observed displacement patterns

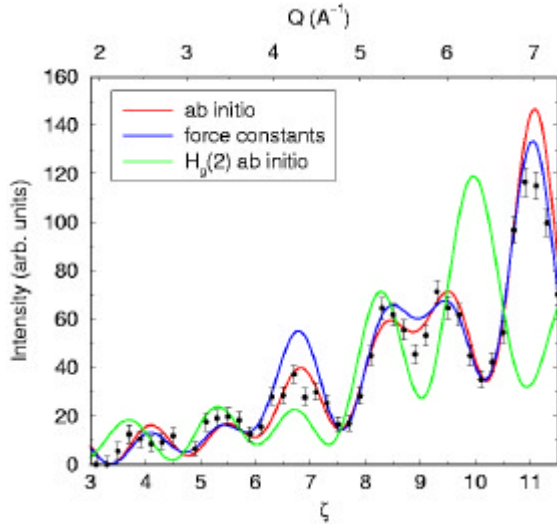is by no means granted even if the frequencies are reproduced correctly.

Figure 2: Intensity of the 33 meV peak versus momentum transfer (z,z,0) observed on a single-crystal sample at T=12 K. The red and blue lines denote the predictions of an ab initio theory (Ref. 4) and of a force-constant model (Ref. 5) for the $H_g(1)$ mode, respectively, and the green line shows the prediction of the ab initio theory for the $H_g(2)$ mode using the same scaling.

The good understanding of the covalent intramolecular forces contrasts with our rather poor understanding of the weak intermolecular forces. From the large distance between atoms on different molecules (≥ 3 Å) it was assumed that these forces are of van der Waals (vdW) type. However, it is known for long that the vdW potential taken from graphite gives a poor account of many properties depending on the intermolecular potential. In particular, the frequencies of the hindered rotations (librations) calculated from the vdW are too low by more than a factor of two [1,2].

In the absence of *ab-initio* calculations for the intermolecular forces, many empirical potentials have been proposed in the literature which were designed to improve the simple vdW ansatz by taking secondary interactions into account. For instance, several models have been developed which include Coulomb forces between charges placed on various locations on the C_{60} molecule. These models reproduce the dispersion of the external vibrations quite satisfactorily[2]. However, a recent experiment of us has shown

that this is true only for the usual phase of C_{60}, where double bonds of one molecule face pentagonal faces of neighbouring molecules. By applying pressure, the C_{60} molecules can be switched to a different orientation, so that double bonds face hexagons. When the pressure is released at low temperatures, the 'hexagon' structure is frozen in. Measurements on this metastable phase have shown that there are surprisingly small differences between the frequencies of the external vibrations in the two phases (see Fig.3), whereas the empirical models predict very large frequency changes (≈50% for the librational modes, upwards or downwards, depending on the model) .

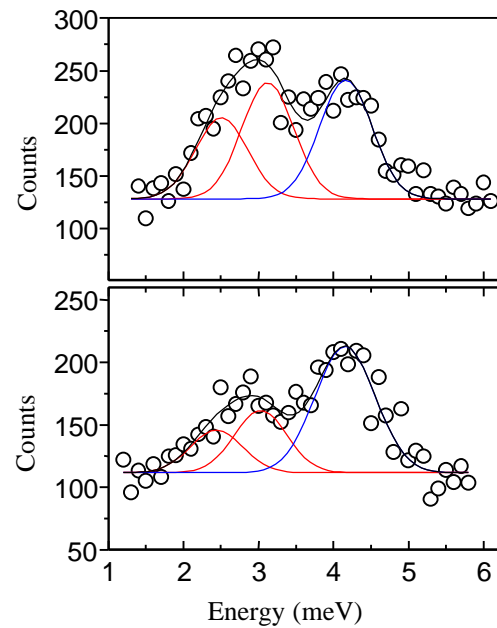*Figure 3: Energy scans taken at Q=(7.5,7.5,0) at T=70 K. The data were fitted with three Gaussians with a width corresponding to the experimental resolution. From model calculations we know that the two low energy peaks correspond to librational excitations and the high energy peak to a translational excitation, respectively. The upper and lower graph refer to measurements on the "pentagon" and the "hexagon" phase, respectively.*

Measurements of the external vibrations at pressures up to 7 kbars are planned in the near future. The results are hoped to advance further our understanding of the intermolecular potential in C_{60}.

References
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