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Inelastic neutron scattering in spectroscopic studies of hydrogen on carbon-supported catalysts-experimental spectra and computed spectra of model systems

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Abstract

Inelastic neutron scattering spectroscopy has been used to observe and characterise hydrogen on the carbon component of a Pt/C catalyst. INS provides the complete vibration spectrum of coronene, regarded as a molecular model of a graphite layer. The vibrational modes are assigned with the aid of ab initio density functional theory calculations and the INS spectra by the a-CLIMAX program. A spectrum for which the H modes of coronene have been computationally suppressed, a carbon-only coronene spectrum, is a better representation of the spectrum of a graphite layer than is coronene itself. Dihydrogen dosing of a Pt/C catalyst caused amplification of the surface modes of carbon, an effect described as H riding on carbon. From the enhancement of the low energy carbon modes ($100\text{--}600\text{ cm}^{-1}$) it is concluded that spillover hydrogen becomes attached to dangling bonds at the edges of graphitic regions of the carbon support.

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1. Introduction

In incoherent inelastic neutron scattering (INS) a fraction of the incident neutrons loses energy by exciting vibrational modes of the scatterer; the INS spectrum is an energy loss spectrum. All molecular vibrations are neutron-active, and in principle observable, because the nuclear interactions are not subject to optical selection rules. The scattering intensity is

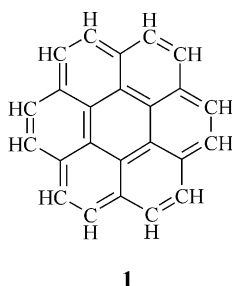
proportional to the concentration of the scatterer and its cross section. Because the scattering cross section is much greater for hydrogen (80 barn) than for any other element (5 barn), displacements involving hydrogen dominate in neutron spectroscopy. The neutron is an ideal probe for the study of hydrogen in catalysts [1]. With the development of the TOSCA spectrometer at ISIS we are able to record the INS spectra of solids and liquids at a resolution approaching that of infrared spectroscopy [2].

There is currently much interest in the spectra and structure of carbon in materials, for example, platinum-on-carbon fuel cell catalysts,

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carbon nanotubes and their interaction with hydrogen. A particular problem is to characterise the carbon: whether amorphous or graphitic, and how disordered. Vibrational infrared and Raman spectroscopy have been much used since graphite and amorphous carbon have characteristic vibrational spectra. Coronene (**1**) has been taken as a one-layer cluster model of the graphite (0001) basal surface [3].



Here we report an experimental and computational study of H species on Pt/C fuel cell catalysts and of model systems including the polynuclear hydrocarbon coronene, $C_{24}H_{12}$, exemplifying our approach to modelling INS spectra.

2. Experimental

Coronene, $C_{24}H_{12}$, (**1**), 99% was bought from Aldrich.

The catalysts was a commercial high loading (40% metal) carbon-supported fuel cell catalyst. The carbon support was a carbon black XC72.

The reduced and evacuated catalysts were dosed at 293 K with pure dihydrogen (99.999%) from a 1.0 l bottle at 1 bar and the dihydrogen uptake was monitored by the pressure change of dihydrogen in the dosing bottle.

INS spectra of the empty sample cell, the carbon support and the dihydrogen-dosed catalysts were recorded at 20 K on the TOSCA spectrometer at the ISIS pulsed neutron source at the Rutherford Appleton Laboratory, Chilton, UK [2]. TOSCA is a high resolution, broad range, inverse geometry spectrometer well suited to the spectroscopy of hydrogenous materials. The energy transfer range is from 16 to 4000 cm^{-1} . The resolution is, $\Delta E/E \sim 2\%$. Spectra were recorded at ca 20 K to freeze the chemistry and

to reduce thermal effects that degrade the spectra. The spectra are presented as the Scattering Law $S(Q, \omega)$ (or function) (S , intensity; Q , momentum transfer and; ω , energy transfer) plotted versus energy transfer.

INS spectra were recorded and dihydrogen dosing carried out using a specially designed cell which made possible scattering of neutrons from carbon without scattering from the catalyst. Pellets of the Pt/C catalyst were arranged in an outer ring within the can. They were outside the neutron beam and in contact with the central mass of carbon support. Only the central section was illuminated with the neutron beam [4].

2.1. Computational modelling

The vibrational spectrum of coronene (**1**) was calculated by the density functional theory (DFT) method using GAUSSIAN 98 with the B3LYP functional and the 6-311G basis set [5]. The vibration frequencies and atom eigenvectors were input to the a-CLIMAX program recently developed for the modelling of INS spectra [6]. A full description of the a-CLIMAX program is available¹. Following conventional practice the calculated spectrum was scaled by 0.83 [7].

3. Results and discussion

3.1. Experimental and computed INS spectrum of coronene

We have measured and calculated the INS of coronene, see Fig. 1. The agreement between the experimental and calculated spectra is good. We are, therefore, confident in our calculations on these and similar systems. For coronene there are 102 fundamental internal modes. Our interest here is not so much in the detailed assignments as in identifying those modes associated with carbon atom displacements that may aid in the interpretation of the spectrum of H on carbon. A table of observed and computed wavenumbers and assignments may be obtained from the corresponding author. The vibrational modes are described as follows:

¹ See the ISIS web site at www.isis.rl.ac.uk.

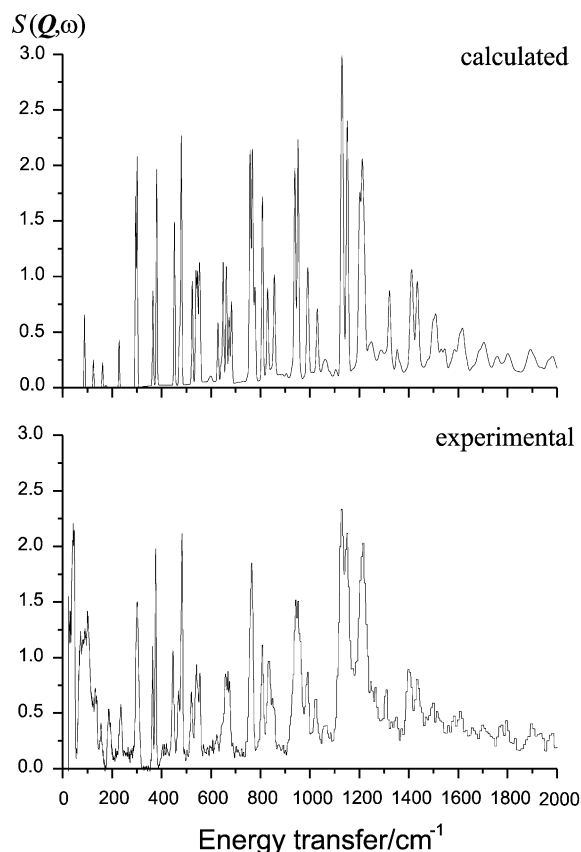


Fig. 1. Computed and experimental inelastic neutron scattering (INS) spectra of coronene.

- Out-of-plane bending and torsional modes of the coronene ring, 90–300 cm^{-1} : predominantly displacements of the edge carbon atoms, the hydrogen atoms moving with the carbon atoms.
- In-plane C–C stretching and breathing modes of the coronene rings (1000, 1230, 1400, 1450, 1600 cm^{-1}): equivalent to the surface modes of a graphite layer.
- C–H bending modes: out-of-plane, 980–1020 cm^{-1} ; in-plane, 1100–1700 cm^{-1}

3.2. Carbon-only vibrational modes of coronene and comparison with graphite

In the a-CLIMAX program it is possible to suppress H modes by assigning to each H atom an infinite mass and a zero scattering cross section. The resulting spectrum is the spectrum due to the carbon atoms and

so models the modes of a graphite layer. The carbon-only experimental and computed coronene spectra, and the INS spectrum of graphite [8] are shown in Fig. 2.

The vibrational Raman and infrared spectra of coronene [3], graphite and carbon have been reported [9]. Recently Papanek et al. [10] in a neutron scattering study of disordered carbon anode materials reported the INS spectrum of coronene. For single crystal hexagonal graphite (space group D_{6h}^4) there is a Raman peak at ca 1580 cm^{-1} , the so-called G-mode (E_{2g} , in-phase stretching and shrinking of the horizontal CC bonds, cf. coronene, 1620 cm^{-1}). In the INS spectrum (Fig. 2) the corresponding peak is part of the broad band near 1500 cm^{-1} . The eigenvector involves in-plane bond stretch motions of pairs of sp^2 carbon atoms. For disordered graphite a peak is observed at 1355 cm^{-1} , the A_{1g} in-plane symmetric breathing mode of the six-member aromatic rings, the D-mode, which is forbidden in perfect graphite. A common force field for graphite and polycyclic hydrocarbons (including coronene) has been proposed [3]. However, we see by comparing Figs. 1 and 2 that the carbon-only INS spectrum of coronene (Fig. 2) is closer to the INS

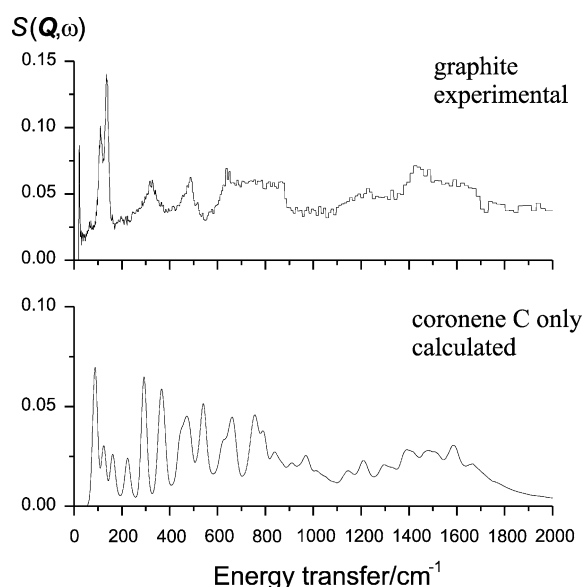


Fig. 2. INS spectrum of graphite and carbon-only INS spectra of coronene. H atom displacements have been suppressed by assigning infinite mass and zero scattering cross section to hydrogen in the a-CLIMAX program. The graphite spectrum is re-plotted from Ref. [8]. These spectra provide better models of a graphite layer than does coronene itself.

of graphite than the coronene spectrum (Fig. 1). In particular the intense bands of coronene between 900 and 1300 cm^{-1} , assigned to C–H out-of-plane and in-plane bending modes, are suppressed in the coronene carbon-only spectrum and, of course, absent from the graphite spectrum.

3.3. INS of a dihydrogen-dosed Pt/C catalyst

We shall discuss elsewhere the chemistry of dihydrogen uptake and spillover on carbon-supported metal catalysts as revealed by INS spectroscopy. In the present paper we wish merely to demonstrate the utility of our experimental and modelling approach to the INS spectra. The INS spectra of a dihydrogen-dosed Pt/C catalyst and carbon-only coronene are compared in Fig. 3. Note

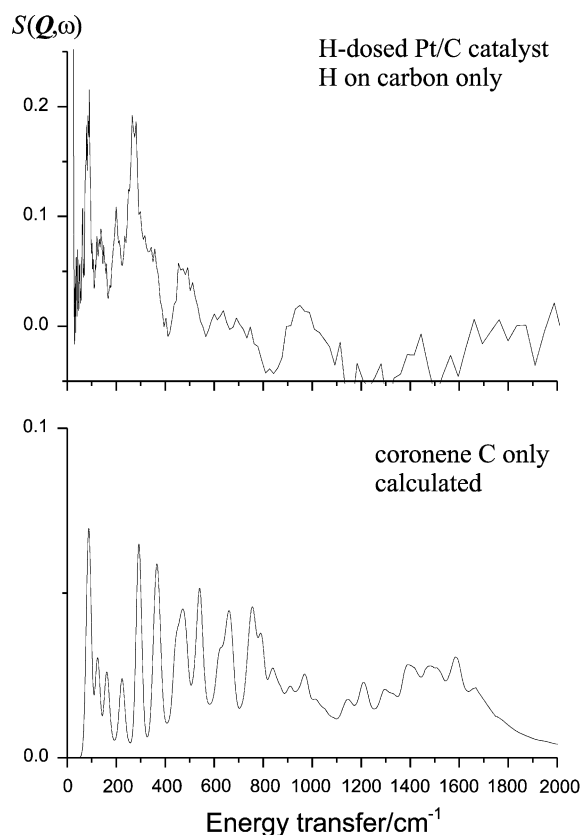


Fig. 3. INS spectra of hydrogen attached to a dihydrogen-dosed Pt/C catalyst and the carbon only INS spectrum of coronene. The H atom frequencies, close to the vibration frequencies of carbon layer are assigned to riding modes of H on carbon, see text.

that the experiment is carried out in such a way that with the Pt/C catalyst only carbon is in the neutron beam and that the spectrum is a difference spectrum, the contributions of the container and the catalyst before dihydrogen dosing having been subtracted. The spectrum is thus due to the presence of hydrogen on the carbon. The interpretation of the INS spectra between ca 100 and 600 cm^{-1} , Fig. 3, is very clear. We see striking similarities in the peak patterns of H on the catalyst and carbon only coronene (Fig. 3) and graphite (Fig. 2). The H atom frequencies are close to the vibration frequencies of the supporting carbon lattice: we are, therefore, observing the riding modes of H on carbon. In these riding modes H atoms move in phase with vibrations of the carbon lattice. The lattice modes are amplified by neutron scattering from the strongly scattering H atoms attached to lattice atoms. The graphite modes that are enhanced and so observed in the spectrum of the H-dosed catalyst are by analogy with coronene assigned to out-of-plane deformations and bending modes. We conclude that spillover H is bound to graphite-like carbon particles at the dangling bonds of edge sites.

4. Conclusions

We have used INS spectroscopy to observe and characterise hydrogen on the carbon component of a Pt/C catalyst. INS provides the complete vibrational spectrum of coronene, regarded as a molecular model of a graphite layer. The vibrational modes are assigned with aid of ab initio DFT calculations and the INS spectra by the a-CLIMAX program. A spectrum for which the H modes of coronene have been computationally suppressed, a carbon-only coronene spectrum, is a better representation of the spectrum of a graphite layer than is coronene itself.

Dihydrogen dosing of a Pt/C catalyst caused amplification of the surface modes of carbon, an effect described as H riding on carbon. From the enhancement of the low energy carbon modes (100–600 cm^{-1}) it is concluded that spillover hydrogen becomes attached to dangling bonds at

the edges of graphitic regions of the carbon support.

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