

NEUTRON INELASTIC SCATTERING AND MOLECULAR MODELLING

M.R. JOHNSON

Institut Laue-Langevin, Grenoble, France

G.J. KEARLEY

Interfacultair Reactor Instituut, Technische Universiteit Delft, Netherlands

H.P. TROMMSDORFF

Laboratoire de Spectrométrie Physique, Université J. Fourier, Grenoble, France

1. INTRODUCTION

From cold neutrons to hot, the range of energies offered by neutron sources covers the whole spectrum of molecular excitations in the electronic ground state. Since spectrometer resolution is a small fraction of the incident neutron energy, excitations down in to the sub μeV range can be measured. The quantum tunnelling of molecular rotors provides the most widespread example of low frequency (sub meV) inelastic excitations [1]. Rotational tunnelling is a wide-amplitude motion connecting rotational configurations of the molecular group, protons typically being exchanged between positions separated by several Å. The shape and amplitude of the potential energy barrier separating stable configurations is probed by the tunnelling motion and the tunnelling probability, which determines the energy of the inelastic excitation, depends exponentially on the barrier. Quantum tunnelling is an extremely sensitive probe of the Van der Waals (VDW), Coulomb and torsional interactions that determine the rotational potential. The value of the probe is seen in the importance of these weak inter and intra-molecular interactions, which determine details of molecular packing in the solid state and conformational flexibility [2] and physical processes which can be thermally activated under ambient conditions, notably for biological molecules [3].

At higher energies, up to ~ 400 meV, molecular vibrations are measured by inelastic neutron scattering (INS). In contrast to tunnelling dynamics, vibrations are small displacements (~ 0.05 Å) of atoms about equilibrium positions. The lowest energy molecular vibrations tend to be torsional in character and, in the case of molecular rotors, they can often be determined from the same rotational potential that governs tunnelling dynamics. With increasing energy, molecular vibrations become less sensitive to inter-molecular VDW and Coulomb interactions, vibrational modes above ~ 50 meV generally being less dependent on the solid state. An important exception to this rule occurs for hydrogen-bonded solids, in which case the frequencies of the bending and stretching modes of hydrogen-bonded protons can change by up to a factor of two compared to the free complex. Tunnelling excitations are similarly sensitive to molecular and solid state structure. Spectroscopy can be regarded as microscopy where the length scale probed is determined by the interaction range (~ 6 Å) and is therefore complementary to diffraction techniques which report average structures over longer length scales.

Hundreds, if not thousands, of INS measurements of quantum tunnelling and molecular vibrations have been accumulated [4]. Spectral peaks can be likened to diffraction peaks in that they are measurements in a reciprocal space (ω and \mathbf{Q}) which makes their interpretation indirect. In-depth data analysis is required to extract the time-dependent (t) evolution of a system about its average structure (\mathbf{r}). However, with such a wealth of spectroscopic data, empirical rules for understanding spectra have been established. But extracting a maximum of information from individual spectra, revealing the subtle effects of the solid state, requires modelling those inter and intra-molecular interactions that determine the potential energy surface (PES) of the molecular system [5].

While experimental techniques have been improving at central neutron facilities, giving better quality data, significant developments have also been made in the field of scientific computing. For computers that have become so powerful that bio-molecules can be simulated on desktop machines, a range of software has evolved allowing scientists to perform different kinds of total energy calculations on molecular systems. These calculations fall into two categories, namely force field and quantum chemistry methods. The former are rapid, parametric methods, which can be applied to large systems (> 1000 atoms) and long timescales (> 1 ns), while the latter determine electronic wavefunctions (or densities) giving higher accuracy for smaller systems.

Total energy calculations can be used in different ways to calculate spectra. Molecular dynamics simulations allow classical particles to evolve in time