

PROBING DISORDER IN CONFINED METHYL IODIDE

The presence of structural disorder in many materials can have a dramatic effect on macroscopic properties. Typically, structural disorder is described in terms of molecular spatial distributions determined from diffraction measurements. A complementary view is to quantify disorder by determining the distribution of potential energies experienced by the molecules. For a highly ordered system the distribution is sharp while it is broad for a disordered system. To explore this approach, high-resolution neutron inelastic scattering has been used to examine the low-energy rotational dynamics of simple symmetric top molecules confined to extremely tiny pores. In effect, the porous substrate furnishes a static impurity distributed throughout the molecular solid that can be thought of as disorder quenched into the molecular matrix. The modification to the rotational spectrum of the confined molecules measured using neutron scattering can then be related to the distribution of potential energies. This measurement technique, known as rotational tunneling spectroscopy [1], is extremely sensitive to the environment experienced by the molecules. By modeling the observed spectra one can quantitatively extract the potential energy distribution.

Rotational tunneling spectroscopy is rooted firmly in quantum mechanics. In a simple picture the potential barrier to reorientation

that, to a good approximation, has three minima determines the motion of a methyl group (a pyramid with a base of three hydrogen atoms having a carbon atom at its apex seen in Fig. 1). In the limit of a small barrier to reorientation, the methyl group can undergo nearly free rotation about the C-I axis. In the limit of a very high barrier, the methyl group can oscillate (librate) within minima. When the temperature is high enough to provide sufficient kinetic energy, the molecule can reorient stochastically by jumping over the barrier, a process known as rotational diffusion. Some molecules such as methyl iodide (CH_3I) possess finite barriers in which the rules of quantum mechanics allow the methyl group to reorient via tunneling *through* the barrier. A schematic illustration of these processes in terms of the potential energy is shown in Fig. 1.

Measurements of the rotational tunneling of methyl iodide (CH_3I) confined to a porous glass with a very narrow pore size distribution (diam $\approx 58 \text{ \AA}$) were performed using the NIST backscattering spectrometer very well suited to such measurements due to its excellent energy resolution: δE (FWHM) $< 1 \mu\text{eV}$. Measurements were carried out for the bulk solid, partially filled pores, and completely filled pores. Spectra taken at 5 K are shown in Fig. 2.

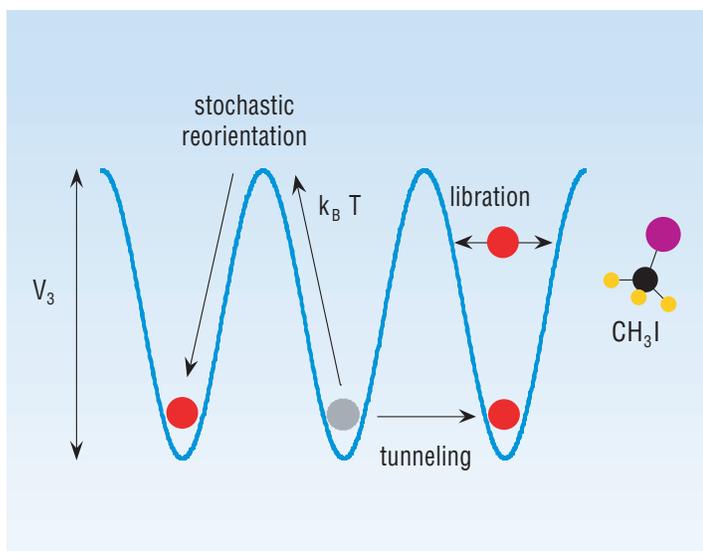


FIGURE 1. Potential energy model for a CH_3 rotor showing the three types of low energy motions observable with neutrons. Note that each circle located in a potential minimum represents one of three particular orientations of the CH_3 methyl group of the CH_3I molecule depicted on the right.

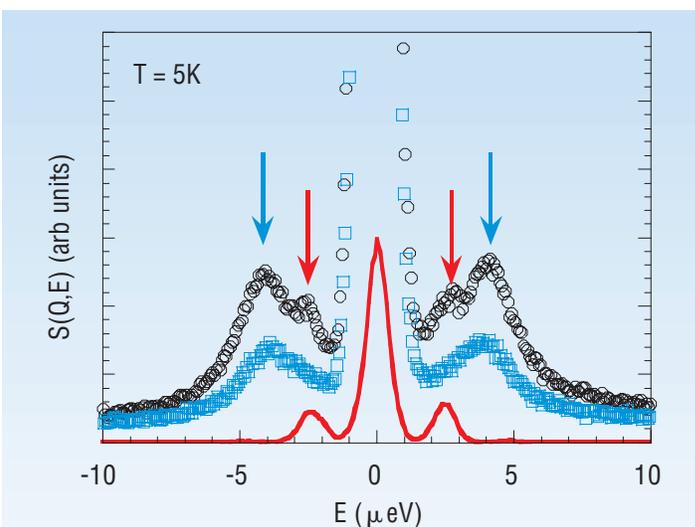


FIGURE 2. Tunneling spectra for the bulk CH_3I (solid red line), partially filled pores (blue squares), and completely filled pores (black circles). Bulk-like peaks (red arrows) indicate strong order while the broad peaks (blue arrows) indicate that disorder is present.

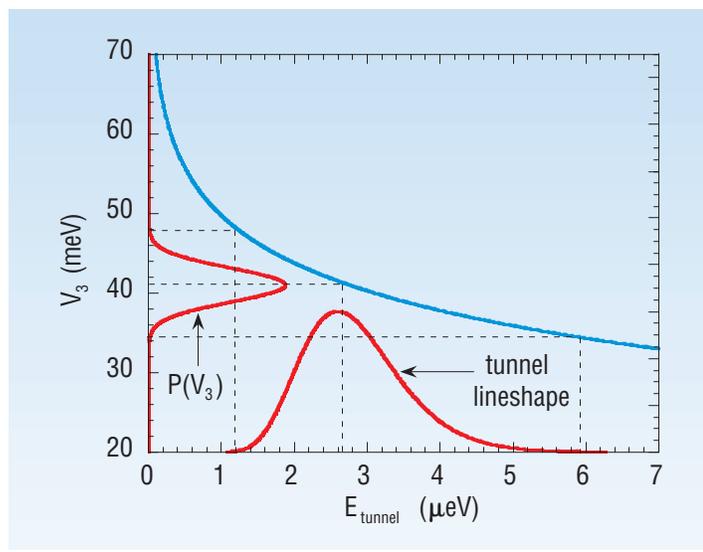


FIGURE 3. Origin of the asymmetric lineshape observed in confined CH₃I. A symmetric distribution of potential barriers yields an asymmetric tunneling lineshape.

The bulk CH₃I spectrum shows two sharp side peaks whose positions are related to the frequency at which the methyl group (CH₃) tunnels between three equivalent orientations. The location of these peaks is directly related to the potential barrier height hindering reorientation. These peaks at $\pm 2.5 \mu\text{eV}$ correspond to a potential barrier of 42 meV. When the pores are partially filled (50 %) a broad set of peaks appear at $\pm 4 \mu\text{eV}$. In addition to these broad peaks, a broad featureless scattering intensity appears underneath the well-defined peaks over the entire dynamic range. When the pores are completely filled the broad peaks at $\pm 4 \mu\text{eV}$ increase in intensity and a new set of peaks at $\pm 2.5 \mu\text{eV}$ appear. We interpret these different peaks as due to the presence of varying amounts of order in the molecular structure of the confined CH₃I. The narrow peaks that occur in the bulk and the full-pore spectra point to the similarity of the potentials experienced by the molecules as expected when there is structural order. The broad peaks at $\pm 4 \mu\text{eV}$ correspond to methyl groups under the influence of a distribution of potential barriers. The very broad scattering feature underlying both the full-pore and partially-filled samples is attributed to very strongly disordered methyl groups. Based on the filling dependence of the two broad scattering components, these are attributed to molecules near the

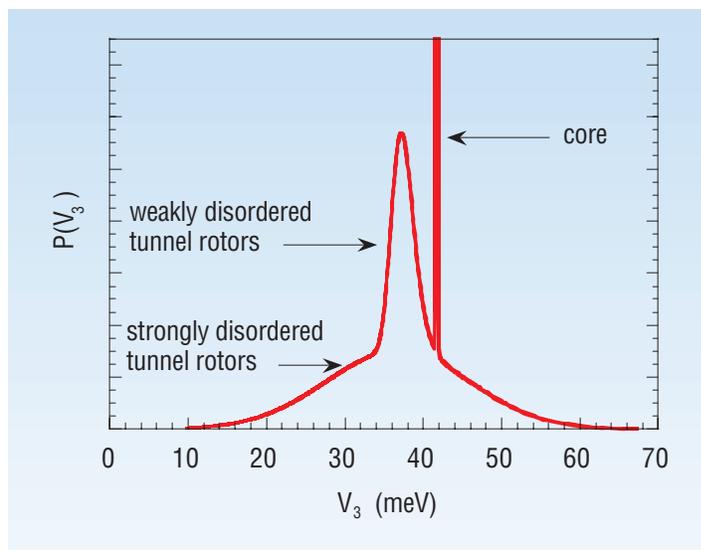


FIGURE 4. The barrier height probability density extracted from full pore tunneling spectra at 5 K.

glass surface while the narrow peaks at $\pm 2.5 \mu\text{eV}$ are due to molecules located near the center of the pore.

To quantify the disorder, we performed numerical calculations of the effects of a distribution of potential barriers on the tunneling lineshape. In Fig. 3 we plot the variation of the potential barrier as a function of tunneling energy. For a broad but symmetric distribution of barrier heights, the tunneling lineshape is clearly asymmetric. Finally, using a relationship between the tunneling energy and barrier height we may extract the probability density for a particular barrier height, $P(V_3)$. The result for the full pore spectra corrected for instrumental resolution is shown in Fig. 4.

Thus neutron inelastic scattering measurements of the rotational tunneling spectrum offer a means of quantifying the disorder of the energy landscape in this system of molecules in a confined geometry. A further challenge is to correlate the energy and structural descriptions of disorder.

REFERENCES

- [1] W. Press, *Single-Particle Rotations in Molecular Crystals*, Springer-Verlag, Berlin, Heidelberg, New York, (1981).