

Low-frequency Molecular Motions of Urea by Neutron-scattering Spectroscopy

By E. O. BODGER and J. W. WHITE

(Physical Chemistry Laboratory, South Parks Road, Oxford)

NEUTRON-SCATTERING SPECTROSCOPY is a tool for studying molecular motions in solids and liquids.^{1,2} It resembles Raman spectroscopy except that a beam of monoenergetic neutrons rather than monochromatic photons is scattered by the molecules. The scattered neutrons may gain or lose quantised amounts of energy to molecular vibrations and rotations (inelastic scattering) or may be scattered elastically with no change in energy as in the Rayleigh scattering of light. Because the neutron excites molecular vibrations in a very different way to light, the selection rules which often restrict optical spectroscopy are relaxed in neutron-scattering spectroscopy and many forbidden rotational and vibrational bands may be seen. The band intensities observed by neutron scattering are directly connected with the amplitudes of the

molecular motions which can be calculated from the spectra. Comparisons with far-infrared data as these become available through Fourier transform spectroscopy³ or other far-infrared techniques will be very interesting. Typically the resolution of the neutron technique is 5–20 wavenumbers in the 5–600 wavenumber regions, but this may be improved by sacrificing neutron intensity.

In our experiments, slow neutrons moderated in liquid hydrogen are used. When scattered by polycrystalline urea at 300° K, the most important inelastic process is energy gain from the quantised molecular modes of the lattice. As different neutrons in the incident monoenergetic group generally gain different amounts of energy from the various modes of the sample the outgoing

neutrons have energies which fall into several groups whose energies differ from one another by the molecular energy state differences. Because this technique is like anti-Stokes Raman spectroscopy the bands in the inelastic spectrum have intensities proportional to the Boltzmann factors and degeneracies governing the populations of the excited molecular vibrational and rotational levels at 300° K.

In the apparatus used⁴ an incident burst of "monoenergetic" cold neutrons fell on the sample of urea in an aluminium can at 300° K. The transmission of the sample was kept above 85% to minimise double-scattering events and the spectrum was recorded at boron trifluoride counters placed at known distances from the sample. The number of neutrons arriving in a series of consecutive 6 μ sec. intervals was plotted against the time of arrival for neutron counters placed at 20, 30, 45, 60, 75, and 90° to the incident beam. If elastically scattered neutrons (whose energy is unchanged) arrive at time t after the burst hits the sample, then those neutrons suffering energy gains through inelastic collisions arrive at time $t - \Delta t_n$. The Δt_n is directly related to the energy gain from the n th molecular quantised state which is equal to the molecular energy level separation. (See Figure 1.)

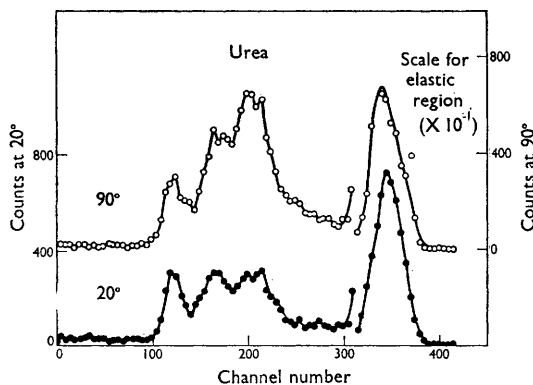


FIGURE 1. Neutron-scattering spectra taken at 20° and 90° scattering angle for urea $\text{CO}(\text{NH}_2)_2$. The elastic peaks are at the right-hand side and for convenience are on one-tenth the ordinate scale shown.

The spectrum of urea and perdeuterourea show particularly well resolved inelastic scattering bands. Figure 1 shows the spectra of urea taken at scattering angles of 20° and 90° from the incident beam. The positions of the peaks can be obtained from these spectra but the intensities are not corrected for the variable efficiency of boron trifluoride

neutron counters at different neutron energies. This correction and averaging over groups of five channels may be done by means of a computer. The resulting spectrum for perdeuterourea is shown in Figure 2 for scattering again at 20° and 90°. The intensity-corrected spectra of both compounds are most similar except for some small frequency shifts.

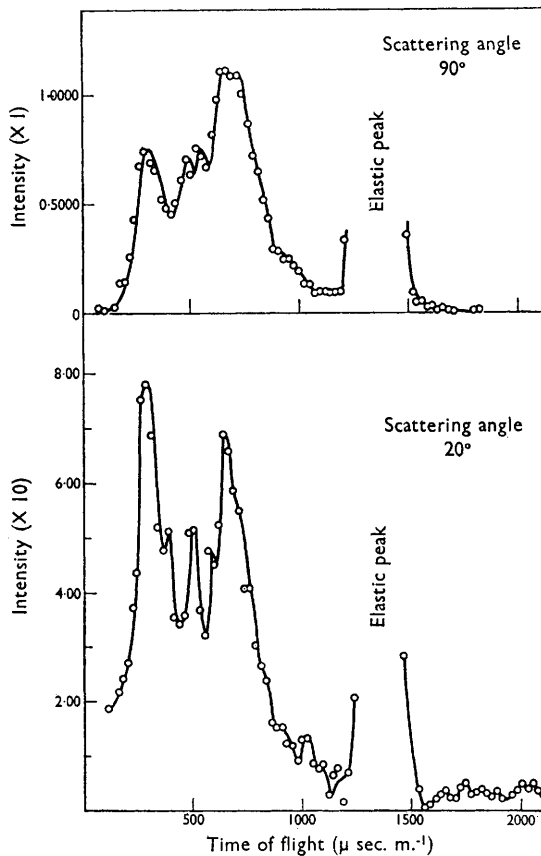


FIGURE 2. Neutron-scattering spectra, taken at 20° and 90° scattering angle to the incident beam, for deuterated urea $\text{CO}(\text{ND}_2)_2$. Only the bases of the elastic peaks are drawn in.

A summary of the band positions with their intensities for the two compounds is given in the Table.

From the angular dependence of the neutron-scattering spectra the mean square amplitudes of these vibrations may also be estimated. Evidence from X-ray crystal studies^{5,6} indicates that these motions are both large and anisotropic being about 2° around the a - b direction and $13.13 \pm 0.47^\circ$ around the c direction. These large displacements

TABLE

Energies and Boltzmann factor-corrected intensities of bands in the low-frequency vibrational spectrum of ureas

Approx. channel number	Urea (Figure 1)			Deuterated urea (Figure 2)			
	Energy transfer (cm.^{-1})	Corrected intensity		Approx. time of flight $\mu\text{sec. m.}^{-1}$	Energy transfer (cm.^{-1})	Correlated relative intensity	
		20°	90°			20°	90°
260	26 ± 1	0.15	0.9	900	38 ± 2	0.23	0.5
210	70 ± 5	1.4	2.8	700	90 ± 5	1.3	2.4
170	145 ± 20	2.1	3.5	500	190 ± 15	1.5	2.3
125	480 ± 80	11	11	330	680 ± 80	30	30

are at least partly responsible for the intensity of the inelastic scattering spectrum.

The frequencies listed in the Table are those of the band group maxima. It is already clear from a comparison of spectra at different scattering angles that there is more structure in the spectra than the Table shows. From the Figures it can be seen that each band maximum contains at least two different bands whose relative intensity depends on scattering angle. The main band positions at different angles are the same.

For both urea and perdeuterourea spectra the relative intensities of the different band groups change greatly with the angle of scattering. In each case the low-frequency region of the spectrum becomes emphasised at high scattering angles. This shows up dramatically in Figures 1 and 2 and also in the relative intensities in the Table, which

have been divided by the Boltzmann factor to normalise for the populations of the scattering states. The band at highest energy transfer does not change much in intensity with angle but for both urea and perdeuterourea the 70—100 cm.^{-1} band doubles in intensity and the 140—200 cm.^{-1} band almost does. Coherent scattering can cause effects like this and would be suspected in perdeuterourea were it not that the phenomena occur to the same extent for urea where incoherent scattering alone is important.

The spectra demonstrate the usefulness of cold neutron scattering spectroscopy for studying the low-energy region of the spectrum and indicate that new information is likely to appear from angular-dependence studies especially as far as infrared data also become available.

(Received, October 28th, 1966; Com. 831.)

¹ J. A. Janik, "Inelastic Scattering of Neutrons", Vol. II, International Atomic Energy Agency (I.A.E.A.), Vienna, 1965, p. 243.

² F. J. Webb and D. G. Pearce, "Inelastic Scattering of Neutrons", Vol. I, I.A.E.A., Vienna, 1963, p. 83.

³ D. Harris, S. J. Cocking, P. A. Egelstaff, and F. J. Webb, ref. 2, p. 107.

⁴ J. Connes, *Rev. Opt. theor.*, 1961, **40**, 45, 116, 171, 231, Translation U.S. Naval Weapons Reports 8099, 1963.

⁵ P. Vaughan and J. Donohue, *Acta Cryst.*, 1952, **5**, 530.

⁶ A. Caron and J. Donohue, *Acta Cryst.*, 1964, **17**, 544.