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L. N. Becka

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Frequency Distribution of Hexamethylenetetramine Crystals

L. N. BECKA* †

Physics Division, Atomic Energy of Canada Limited, Chalk River, Ontario, Canada

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The energy distribution of neutrons inelastically scattered from hexamethylenetetramine powder at 80° and 300°K is given. Features of the scattering curve are described and interpreted in the light of a simple model of the lattice vibration spectrum.

HEXAMETHYLENETETRAMINE (hereafter HMT) is an exceptionally suitable substance with which to study the lattice vibrations of molecular crystals. The crystal has cubic symmetry ($\bar{I}43m$) and a very simple structure (one molecule per primitive cell), the molecules of HMT are nearly spherical and there is no phase transition below the melting point (many other crystals of nearly spherical molecules exhibit solid-phase transitions).

A simple model for the vibration spectrum of HMT has been proposed and data dependent on the lattice dynamics have been analyzed in terms of this model.¹ The data consisted of elastic constants,² Raman spectrum,³ entropies,⁴ and temperature variations of mean-square amplitudes of vibration.¹ The model separates the modes into six external (intermolecular) and sixty internal (intramolecular) modes. The external modes are represented by a triply degenerate optical branch with an Einstein distribution and by an acoustical branch with a Debye distribution. Furthermore, the external optical modes are assumed to be pure librations and the acoustical modes pure translations. The characteristic frequencies of the external optical and acoustical modes ν_E and ν_D , respectively, were determined from the amplitudes of vibration at 298°K as $h\nu_D = 9.0$ milli-eV (hereafter meV) (72.6 cm^{-1}) and $h\nu_E = 5.5$ meV (44.4 cm^{-1}). These values agree well with those suggested by the spectroscopic and calorimetric measurements. The calculated entropy function and the predicted temperature dependence of the vibration amplitudes are very close to their empirical values.

Direct information on the frequency distribution has been obtained with neutron inelastic-scattering experiments. Figure 1 shows the intensity vs scattered-neutron-wavelength patterns of HMT powder at 80° and 300°K, obtained using the Chalk River rotating

crystal spectrometer.⁵ The measurements were made in the symmetrical transmission position at a scattering

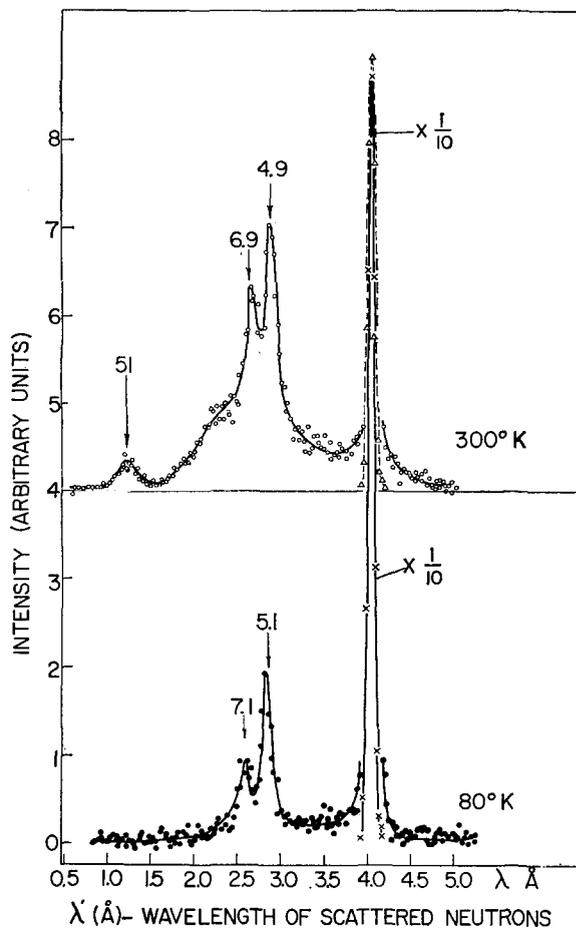


FIG. 1. Plot of intensity vs scattered-neutron wavelength of hexamethylenetetramine powder at 80° and 300°K. The positions of the peaks are given in milli electron volts.

angle of 111 degrees with a specimen of 71% transmission.

The 300°K pattern has a very sharp peak at 4.9

* Visiting National Research Council Fellow from Buenos Aires, Argentina.

† Present address: Department of Inorganic & Physical Chemistry, Facultad de Ciencias Exactas y Naturales, Peru 222, Buenos Aires, Argentina.

¹ L. N. Becka and D. W. J. Cruickshank (to be published).

² S. Haussühl, *Acta Cryst.* **11**, 58 (1958); G. M. Ramachandran and W. A. Wooster, *ibid.* **4**, 431 (1951).

³ L. Couture-Mathieu, J. P. Mathieu, J. Cremer, and H. Poulet, *J. chim. phys.* **48**, 1 (1951).

⁴ Shu-Sing Chang and E. F. Westrum, *J. Phys. Chem.* **64**, 1547 (1960).

⁵ B. N. Brockhouse, Paper I/S 18, International Atomic Energy Agency Symposium on Inelastic Scattering by Solids and Liquids, Vienna, October 11-14, 1960. Issued as Chalk River Rept. CRNP 947, AECL 1183.

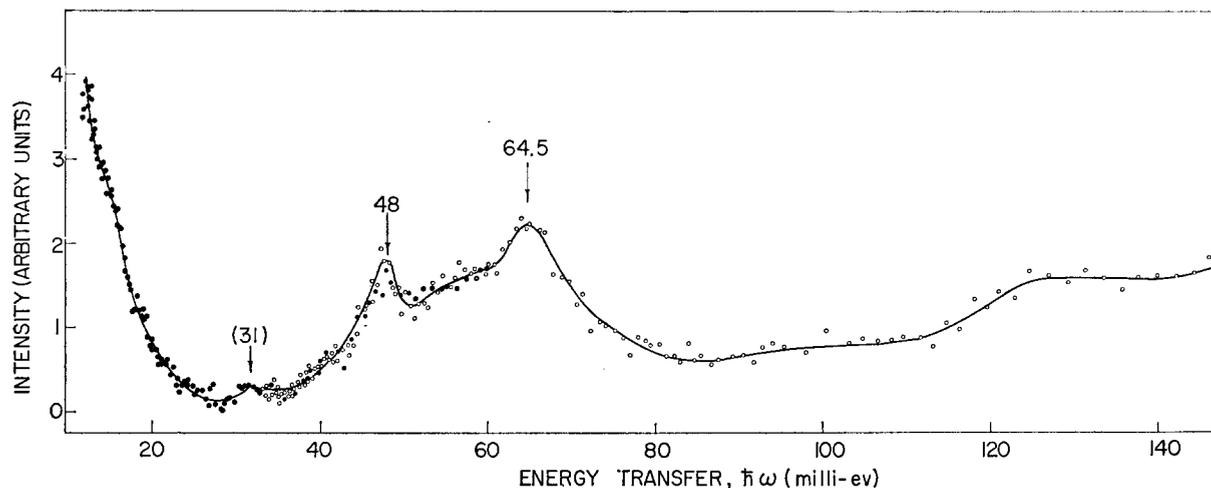


FIG. 2. Plot of intensity vs energy transfer of scattered neutrons of hexamethylenetetramine powder at 300°K. The positions of the peaks are given in milli electron volts. The small peak at 31 meV appears also with empty sample holder.

meV (39.5 cm^{-1}) that corresponds very nicely with $h\nu_E$; the sharp peak at 6.9 meV (55.7 cm^{-1}) could be due to splitting in the external optical branch or to a very flat acoustical branch; the broad-peaked region underneath the sharp peaks is probably due to the acoustical modes. The peak at 51 meV (411 cm^{-1}) is probably due to some internal modes. The valley between the low-frequency region and the peak at 51 meV indicates there is little mixing between internal and external modes. The 80°K pattern has two sharp peaks at 5.1 meV (41.1 cm^{-1}) and 7.1 meV (57.3 cm^{-1}), showing a shift of $+0.2 \text{ meV}$ ($+1.6 \text{ cm}^{-1}$) in the position of the corresponding peaks at 300°K. This shift is of the same sign and order of magnitude as the anharmonicity correction to ν_D and ν_E previously assumed¹ in calculating the entropy function. As expected, higher frequency modes are not excited at 80°K, and so the intensity falls to zero after the peak at 7.1 meV.

Figure 2 shows the intensity vs energy-transfer patterns obtained with HMT powder at 300°K using a crystal spectrometer in the beryllium detector method.⁶

⁶ A. D. B. Woods, B. N. Brockhouse, M. Sakamoto, and R. N. Sinclair, Paper I/S 22 of I.A.E.A. Symposium (see reference 5). Issued as Chalk River Rept. CRNP 948, AECL 1088.

The peaks at 48 meV (385 cm^{-1}), 64.5 meV (520 cm^{-1}), and the region between them correspond well to the lower internal frequencies observed and calculated by Couture-Mathieu *et al.*³ [the lowest internal mode has a calculated $h\nu = 43 \pm 5 \text{ meV}$ ($347 \pm 40 \text{ cm}^{-1}$), and is inactive in Raman and infrared]. Again it is seen that there are no normal modes in the frequency region between the internal and external modes.

Discrepancies between the observed frequency distribution and that predicted by the simple model are evident in the high cutoff of the acoustical spectrum and in the existence of two sharp peaks instead of just one. The model is inadequate for reproducing the actual distribution, but very good for evaluating properties depending on integration over the frequency distribution.

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