MOLECULAR CRYSTAL LATTICE AND ITS EXCITED STATES

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The model of a molecular crystal based on the concept of a molecule as a rigid entity is considered. The collective excitations in a model of this kind include phonons, rotons, librons, and retarded torsional vibrations. Experiments exemplifying these collective excitations are indicated. Experiments based on neutron spectrometry are chiefly considered. The prospects of studying molecular crystals in these and other ways are discussed.

INTRODUCTION

A crystal lattice is essentially a "vacuum" containing a kind of quantized space, i.e., a vacuum in which (if we use the concept of the reciprocal lattice) only points (h, k, l) with integral values of h, k, and l can exist. The elastic scattering of radiation in this vacuum may take place entirely coherently, involving exchange by virtue of the reciprocal-lattice vector τ_{hkl}, or in other words the exchange of a particle with the quantum numbers of the vacuum. Inelastic scattering processes may also take place coherently in this vacuum, and then, in addition to exchange of the vector τ_{hkl} certain objects usually known as quasi-particle, for example, phonons, are formed.

It is interesting to note that there is quite a close analogy between the foregoing representation and the phenomena which take place in the coherent processes associated with so-called strong interactions. The elastic coherent scattering of a hadron by a hadron (for example, a proton by a proton) is also described in terms of the exchange of a particle with the quantum numbers of the vacuum (a pomeron); as in the previous case the vacuum is to be understood as the ground state of the interacting fields. In this case it is not the quantization of the space but that of other quantities, such as the baryon number, the z component of the isospin, and so on, which is important. The analogy is even more complete than this, since, in the case of strong interactions, coherent, inelastic processes also exist, in which, in addition to the exchange of a pomeron, particles such as pions, kaons, etc., are formed [1].

Let us return, however, to the crystal lattice. Quasi-particles such as, for example, phonons, constitute the excited states of the lattice; their properties are of course related to the type of interactions involved, i.e., with the nature of the crystal field, the character of the symmetry, and the possible laws of conservation arising from this. Usually in such substances as metals the crystal field is described phenomenologically by means of various force parameters, which are determined by fitting theory to experimental data. The parameters so obtained enable us to find the characteristics of the phonons constituting the excited states in these materials.

In molecular crystals, the interactions may either be approximated by electrostatic multipole-multipole interactions or else described by phenomenological force parameters, universal for a wide range of substances. Intermolecular interactions generate several types of collective excitations (quasi-particles) with different lifetimes. These include phonons, rotons, librons, and retarded torsional vibrations (rotations).

Institute of Nuclear Physics, Poland. Translated from Problemy Fiziki Élementarnykh Chastits i Atomnogo Yadra, Vol. 2, No. 4, pp. 1061-1074, 1972.

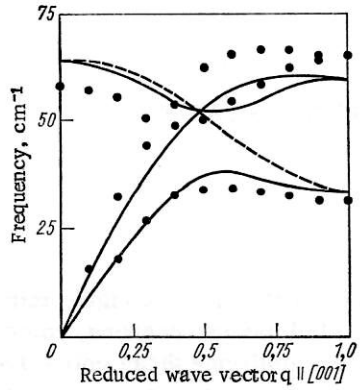

Fig. 1

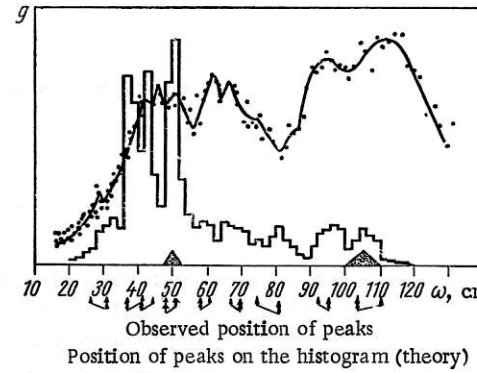

Fig. 2

Fig. 1. Experimental dispersion curves for hexamethylenetetramine [3], and those calculated on the basis of the Kitaigorodskii model.

Fig. 2. Comparison between the function $g(\omega)$ calculated for acenaphthene at 80°K on the basis of the Kitaigorodskii model and that determined experimentally by inelastic neutron scattering. The histogram gives the theoretical solution. The arrows indicate the observed and expected positions of the peaks. The triangles show the energy resolution $\Delta\omega$ [4].

1. PHONONS IN THE MOLECULAR LATTICE

A molecular crystal [2] may be considered as a crystal in which two types of forces are acting; these forces differ, at any rate, in magnitude. The stronger forces connect the atoms into groups (molecules) and the weaker forces hold these groups together. In order to study the dynamics of the molecular crystals, we may, to a first approximation, accept that the molecules move in the crystal as solid particles. We may then proceed in three ways. First, we may set up the dynamics of molecular crystals purely phenomenologically, on the example of atomic crystals, i.e., represent the interaction potential between the molecules in the form of a series in powers of deviations from the equilibrium position, solve the equations of motion, and find the dispersion curves, expressing these in terms of force constants. The number of these constants and also their actual values are then found by fitting the theory to experimental data. Second, we may describe the dynamics in terms of electric multipole interaction between the molecules. In this case the number of parameters to be fitted to the experimental data is quite small. These parameters include the multipole moments and the polarizabilities of the molecules. Third, the interaction between the molecules may be described with the help of a phenomenological potential constituting the sum of paired phenomenological interaction potentials between individual atoms belonging to different molecules:

$$U(r)=\sum_i V_i(r)=\sum_i\left[-\frac{A_i}{r^6}+B_i\exp(-\alpha_i r)\right],$$

where U(r) is the interaction potential between the molecules, $V_i(r)$ is the paired interaction potential of the i-th pair of atoms belonging to different molecules, and the summation is carried out over all possible pairs. A very interesting hypothesis was proposed by A. I. Kitaigorodskii [3], who considered that the constants A_i, B_i, α_i relating to a specified pair were universal for all crystals with different molecules. The values of these universal constants were derived by Kitaigordskii from thermodynamic data for a large number of molecular crystals. As an example we present the Kitaigordskii constants for three types of pairs in Table 1.

At the present time very few experimental data relating to inelastic coherent neutron scattering are available for molecular crystals. However, this method has been applied to a few substances. Dispersion curves have been obtained for hexamethylenetetramine $C_6N_4D_{12}$ [2]. The experimental results and theoretical curves calculated by means of the Kitaigorodskii potential are shown in Fig. 1. The agreement is quite good.*

* It should nevertheless be mentioned that in his calculations the author replaced the value of the A(H...H) constant 57 kcal/(mole · Å^{-6}) by 164 kcal/(mole · Å^{-6}).

TABLE 1

Pair of atoms	A, kcal/(mole · Å^{-6})	B, kcal/mole	β, Å^{-1}
C...C	358	42 000	3,58
C...H	154	42 000	4,12
H...H	57	420 000	4,86

The Polish group in Dubna studied inelastic coherent neutron scattering by acenaphthene [4] and obtained the frequency spectrum $g(\omega)$. The results of the theoretical calculation and experimental measurements are presented in Fig. 2. The calculation was based on dispersion curves obtained by means of the Kitaigordskii table. The positions of the theoretical and experimental maxima coincide, although the intensities fail to agree, this probably being due to the omission of the polarization factor $(\xi, Q)^2$ and also two-phonon processes.

These examples should stimulate further investigations, both theoretical (in the sense of analyzing new models) and experimental, in the sense of perfecting methods of studying inelastic coherent and incoherent neutron scattering.

2. ROTONS

In interpreting the optical spectra of solid parahydrogen, Van Kranendonk [5] directed attention to the fact that, in molecular crystals, the rotational motion of a certain group of molecules might sometimes be described by a "rotational quantum number" J. In these cases the forces acting between the centers of gravity of the molecules and determining the structure of the crystal retard the translational motion but have little effect on the rotation of the molecules. Here we are considering free rotation in contrast to the frequently employed term "retarded rotation." However, the effect of the crystal field is nevertheless one of producing interaction between molecules with a "rotational quantum number" J, so that rotational excitations pass from one molecule to another. This situation is reminiscent of an exciton. The term "exciton" does not here involve electron excitations but simply means the transfer of excitation from one molecule to another and so on. Van Kranendonk introduced the term "rotational exciton" or "roton." This kind of excitation may be identified with the concept of a quasi-particle by analogy with the case of lattice vibrations.

If interaction through the crystal field is very weak, then the J levels give plane "dispersion curves" in (ω, q) space. In general, however, excitations of the roton type are characterized by dispersion, and this leads to a certain broadening of the rotational peaks in the frequency-distribution spectrum $g(\omega)$.

After these general comments, let us turn to solid parahydrogen. The total nuclear spin for a molecule of parahydrogen is equal to zero. The fundamental rotational state of the molecules $J = 0$. In the first perturbed rotational state one of the molecules is in the state $J = 2$. We may consider that this state is not concentrated in a localized manner in a single molecule, but is transferred from one molecule to another in the form of a roton as a result of interaction (probably of the quadrupole-quadrupole type). The broadening of the roton peak in the function $g(\omega)$ due to dispersion may be observed by optical methods if a two-exciton process is employed, this not being restricted simply to the region $q = 0$. The infrared spectrum of solid p-H_2 obtained by Gush et al. [6] is shown in Fig. 3. We observe a wide band, corresponding to the formation of two excitons: a vibron (internal vibrations in the H_2 molecule) and a roton $J = 2$. The width of the band is about 20 cm^{-1} (the distance between the levels $J = 0$ and $J = 2$ equals 356 cm^{-1}) and is the result of interaction between the molecules, i.e., transfers (transitions) of roton excitation.

The foregoing example shows that, in order to find the dispersion of the rotons as well as merely detecting them, it is essential to improve the energy resolution of the inelastic neutron-scattering methods employed very considerably.

The study of rotons in crystals is still in its early stages. Rotons have only been detected in p-H_2 [6], solid methane [7], and certain clathrates [8].

We may mention one further example studied by the Polish group in Dubna. This relates to solid NH_4ClO_4 [9]. The function $g(\omega)$ obtained by inelastic, incoherent neutron scattering is given in Fig. 4. Rota-

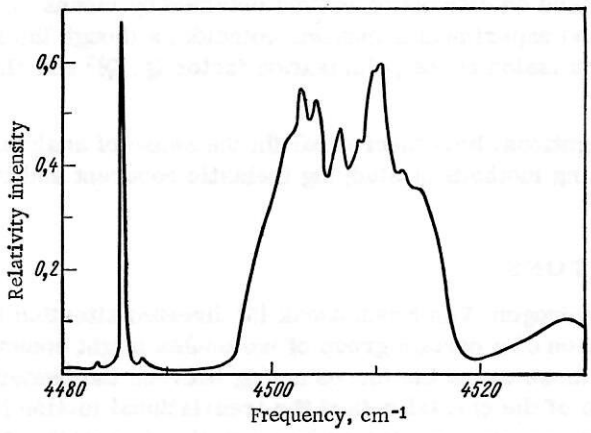

Fig. 3

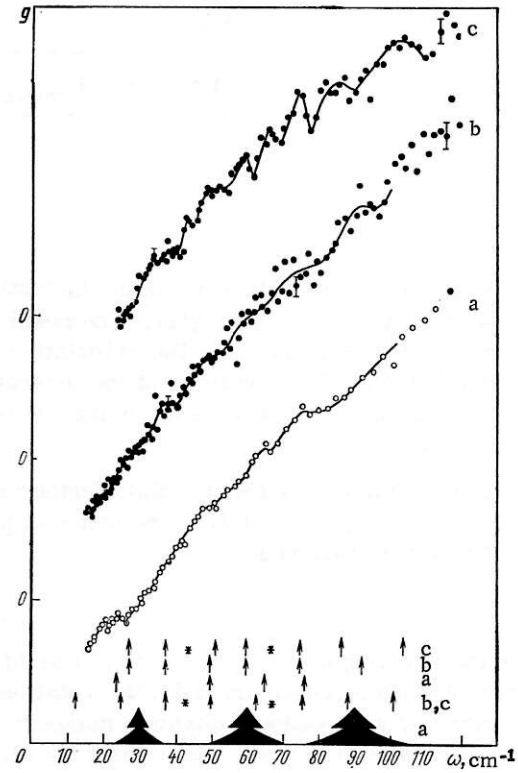

Fig. 4

Fig. 3. Infrared absorption spectrum of solid p-H_2 [6]. The wide band is a combination band for two excitations: $\nu = 1$ (vibron) and $J = 2$ (roton) [5].

Fig. 4. Low-energy part of the function $g(\omega)$ for solid NH_4ClO_4 [9]: a) results obtained in Brookhaven (90°K); b) results obtained in Dubna (second series), 80°K; c) results obtained in Dubna (first series), 113°K. In the lower line the arrows indicate the expected rotational peaks and the asterisks indicate the translational vibrations. The distance between the rotational peaks is 12.6 cm^{-1}. Row (a): peaks observed in experiment a; row (b); peaks observed in experiment b; (compare distance 12.9 cm^{-1}); row (c): peaks observed in experiment (c) (compare distance 12.6 cm^{-1}). Triangles: lower: resolving power in experiment (a); upper: resolving power in experiments (b) and (c).

tional peaks are clearly evident. The resolving power in the neighborhood of the peaks is about 6%, so that it is scarecely capable of doing more than simply detect them. As regards the widths of the peaks, i.e., the widths of the roton bands, little can as yet be said about these.

Systematic and worthwhile investigations into this kind of excitations capable of providing information regarding intermolecular interactions in crystals will clearly only become possible if the resolving power can be made better than approximately 0.5%.

3. LIBRONS

In contrast to parahydrogen, orthohydrogen has a nuclear spin $I = 1$, so that at the lowest rotational level it has a momentum J equal to unity and not zero as in parahydrogen. Close to 0°K solid orthohydrogen probably has a face-centered cubic lattice structure* with four sublattices. In each sublattice, H_2 quadrupoles lie along one of the four diagonals of the cube. The lowest state of any given sublattice corresponds (in the semiclassical approach) to the case in which the z component of J in the direction of the

* However, there are also weighty arguments in favor of a hexagonal close-packed structure.

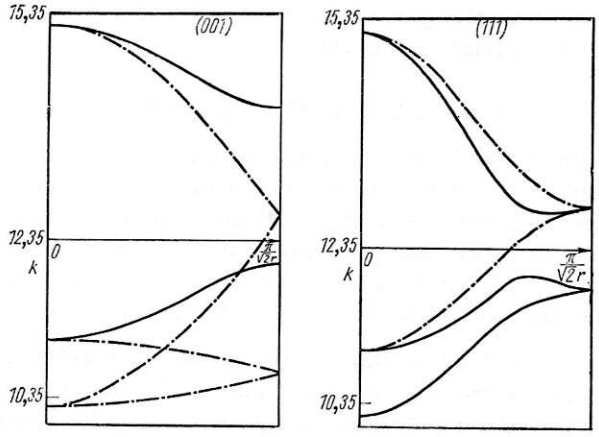

Fig. 5

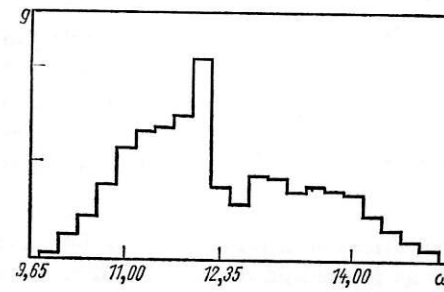

Fig. 6

Fig. 5. Dispersion curves of librons in ortho-H_2 in the [111] and [001] directions [10]: k = Boltzmann's constant, taken as unity of energy; r = distance between the molecules.

Fig. 6. Libron part of the function $g(\omega)$ for ortho-H_2 [10] (ω is expressed in units of the Boltzmann constant k).

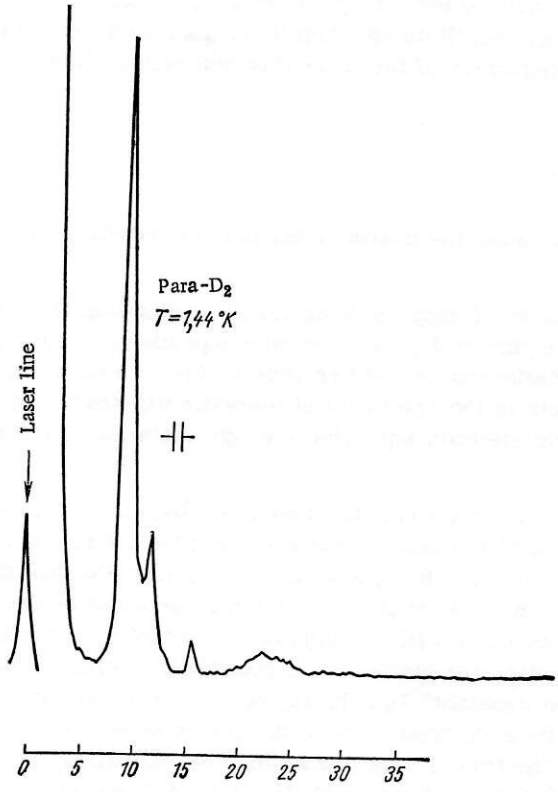

Fig. 7. Raman scattering of light associated with libron excitations in para-D_2 [11].

quadrupoles equals zero ($J_z = 0$), i.e., the rotational moment of the molecule is directed perpendicularly to the diagonal in question.

As indicated by Homma et al. [10], this system incorporates excitations very similar to spin waves in antiferromagnetics. These arise when the vector J acquires a nonzero, integral projection in the direction of the quadrupoles. From the semiclassical point of view a wave-like transfer of precession thereupon takes place, with a constant phase shift from one molecule of the sublattice to another. By using the quadrupole-quadrupole interaction we may construct operators corresponding to the generation and annihilation of excitations and call them librons (new quasi-particles).

We should further mention that, whereas the formation of the rotons mentioned in the previous section involved transitions of ΔJ, the formation of the librons involves transitions of ΔJ_z.

The dispersion curves calculated by Homma and others [10] for the librons in ortho-H_2 are shown in Fig. 5; the spectrum of libron states, i.e., the function $g(\omega)$, is presented in Fig. 6. We see that the function $g(\omega)$ of these excitations has a maximum in the region of 1 meV, i.e., considerably lower than the roton peaks.

So far no librons have been detected experimentally in ortho-H_2. The theory of libron states may be extended, however, to p-D_2, in which a libron peak has been detected experimentally in Raman light scattering [11] (Fig. 7).

The problem of experimentally verifying the libron dispersion curves obtained on the basis of quadrupole interaction remains open. This verification is only feasible by using coherent, inelastic neutron

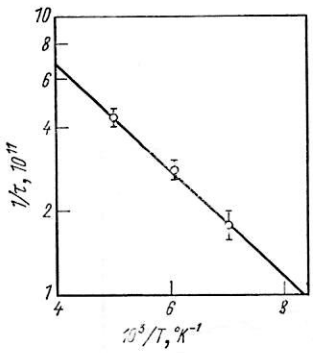

Fig. 8. Probability of a jump $1/\tau$ (sec^{-1}) as a function of reciprocal temperature in neopentane [12].

scattering. It is also interesting to study other molecular crystals in the hope of detecting libron excitations in these.

4. RETARDED ROTATION

It was shown in Section 1 that, on neglecting the internal motions occurring in molecules, the dynamics of a molecular crystal reduce to the vibrations of the molecules as a whole. If we neglect the interaction between rotation and translations, these vibrations may be divided into translational and rotational types. We shall now discuss certain aspects of the rotational vibrations of retarded rotations.

Of course, from the formal point of view, phonons of retarded rotations may be derived from the harmonic approximation by assuming a parabolic dependence of the potential energy on the angular displacement of the molecule from the equilibrium position. However, a parabolic relationship is an inadequate approximation for present purposes, since the potential energy should be a periodic function of the angle. A better approximation is given by a sinusoidal dependence on the angle of deviation. This type of potential leads to spontaneous jumps of the molecules through the barriers between the minima. In the language of quantum mechanics, this means that the rotational phonons only live for a finite time, and the formal reason for their decay is concealed in anharmonism.

If the barrier between the potential-energy minima is not too low, the process takes place as follows: for a certain average time τ the molecule executes rotational oscillations, then it makes a jump into another equilibrium position, and so on. The temperature dependence of the time τ is determined by the relation

$$\tau = \tau_0 e^{\frac{U_{act}}{kT}}.$$

By measuring this relationship experimentally we may determine the height of the barrier retarding the rotation U_{act}.

There are a number of methods of measuring the time τ: It may be determined by studying the temperature dependence of the width of the magnetic-resonance line or the temperature dependence of the magnetic-resonance relaxation time, from the phenomenon of dielectric relaxation (particularly in the microwave region), or by measuring the broadening of the maxima in the spectrum of inelastically scattered neutrons. It should nevertheless be mentioned that all these methods only give a rough estimate of the barrier rather than determining it to a high accuracy.

Let us now consider the neutron method. Disordered jumps through the rotational barrier cause a broadening of the phonon peaks in the spectrum of inelastically scattered neutrons, and also cause the broadening of the elastic maximum, which acquires a Lorentz form. The foregoing model of jumps through the barrier leads to a relationship between the line width and time τ, so that by measuring the width of the quasielastic peak we may determine the time τ. It should be noted that quasielastic broadening may also be obtained on the basis of another model, that is, by assuming, not jumps, but a rotational motion of the Brownian type, with a certain constant "rotational-diffusion constant" D_r. In any real case the situation is probably more complicated, and will have to be described by a superposition of the two models. An example of an investigation in which the temperature dependence of the time τ was determined by measuring the broadening of the quasielastic neutron-scattering peak is that of Lechner et al. [12] on solid neopentane. The resultant relationship is illustrated in Fig. 8, and leads to a barrier height of U_{act} = 0.88 kcal/mole. Nuclear magnetic resonance gives a value of U_{act} = 1.0 kcal/mole.

Apart from ordinary crystals, the method of quasielastic neutron scattering enables us to study amorphous materials containing complex molecules. After a resolution of better than 0.5% has been achieved, the prospects of this method should extend still further, enabling a variety of effects leading to a quasielastic broadening to be distinguished and identified.

CONCLUSIONS

We see from the foregoing discussion that the study of the excited states of molecular crystals is still in its infancy. Even in the case most accessible for investigation, that of phonon excitations, the majority of the experimental material relates to the frequency-distribution function (phonon spectrum) and not to the more informative dispersion curves. On the other hand, a further theoretical development of the dynamics of molecular crystals based on comparatively simple interactions is also called for. It is therefore most desirable to measure the phonon dispersion curves in order to discover whether the interaction within the molecular crystals in fact has a multipole character and is universal for any particular pair of atoms.

We have seen that the greatest amount of information regarding the type of interactions may be obtained by studying roton and vibron excitations. Here both theoretical and experimental material is very sparse. However, the energy resolution of neutron spectrometers will probably improve over the next few years in the region of cold and thermal neutrons. Investigations into this kind of excitations will then increase substantially. The dispersion curves of rotons and librons will be measured, together with the corresponding lifetimes.

With the improved resolving power, measurements of quasielastic neutron scattering should in future provide very rich material relating to a variety of diffusion effects and also effects associated with jumps through an activation barrier.

It should be noted that, in molecular-crystal investigations of this kind, it is vital that complex measurements should be made on each specific material by a variety of methods. The method of inelastic neutron scattering should be used in conjunction with other no less important methods: nuclear magnetic resonance, infrared absorption, Raman scattering, calorimetric measurements of the frequency dependence of the dielectric constant over a wide frequency range.

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