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Acoustical Absorption Arising from Molecular Resonance in Solids*

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Resonance phenomena resulting in anomalously high acoustic absorption can occur whenever lattice and internal molecular vibrational frequencies overlap. Significant effects are predicted at all acoustic frequencies, without restriction to the resonance region. A method is given for calculating resonance absorption using available molecular constants. As an illustrative example, the magnitude of resonance absorption has been calculated for benzene. The predicted absorption is 0.5 cm^{-1} at the 10-Mc/sec frequency, orders of magnitude larger than have been observed in other single crystals. In order to test this prediction, measurements of absorption were made on a large single crystal of benzene yielding at 10 Mc/sec, 0.25 cm^{-1}. This agreement between absorption and calculated values is considered adequate, confirming the phenomenon.

INTRODUCTION

A MOLECULAR crystal exhibits two classes of thermal oscillations: those in which each molecule vibrates as a whole about its lattice position; and the internal vibrations of the atoms comprising the molecule. Although lattice vibrational frequencies are generally lower than internal vibrations, it is quite possible that higher lattice vibrational frequencies may overlap the gravest internal vibrational mode. Because some coupling always exists between these vibrational modes, an overlap in frequency results in resonance. One of the concomitant phenomena in mechanically resonant systems is the slow transfer of energy. For example, two weakly coupled pendula exchange oscillations only if they are close to resonance; but the closer to resonance, the slower the exchange of energy. Similarly, the rate of energy transfer between lattice and internal oscillations is slow; and thermal equilibrium is achieved relatively slowly.

Crystalline substances possessing this resonance property should exhibit the phenomenon of a time-dependent specific heat. In particular, for a periodic temperature variation of frequency ω, the specific heat will be of the form, $c=c_0+c'/(1+i\omega/\kappa)$; the parameter, κ, is the number of transitions per unit time; its reciprocal is the relaxation time of the process. The complex character of c expresses the phase lag between the applied temperature and internal thermal oscillations; the real part of the specific heat is in phase with the temperature while the imaginary part lags by $\pi/2$.

A substance having a complex specific heat also has a complex velocity of sound; stated in another way, the wave number of an acoustical wave will be complex. Since the imaginary part of the wave number is the negative of the absorption coefficient, it can be shown that absorption is given by[1]

$$\alpha=\frac{1}{2V}\frac{(c_p-c_v)}{c_p}\frac{c'}{(c_p-c')}\frac{\omega^2\kappa}{(\omega^2+\kappa^2)},\tag{1}$$

where V is the velocity of sound.

Acoustical frequencies are always much smaller than the transition rate κ; hence the magnitude of the absorption will be inversely proportional to κ. Referring again to the two-pendula model, it is apparent that the weaker the coupling, the slower the rate of energy exchange. Hence, the acoustical manifestations of this phenomenon should be most apparent in molecules having weak coupling between lattice and internal vibrations.

The coupling of internal and lattice vibrations has been used by Pauli, Born, and others to explain the broadening of optical absorption lines in crystals at the dispersion frequency[2] and as an explanation of thermal conductivity in electrical insulators.[3] However, the possibility that mode coupling could be strongly manifested in acoustic absorption appears to have been overlooked. Landau and his colleagues[4] did consider the case of acoustic absorption resulting from coupling of the acoustic wave with the lattice vibrations, but this is a negligible effect except at extreme ultrasonic frequencies.

The ensuing discussion gives a method for the prediction of acoustic absorption in actual molecular crystals. It is shown that resonance absorption is not a negligible effect in molecular solids but can be orders of magnitude larger than other absorptive processes; as a confirming example, experimental observations on crystalline benzene are presented.

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[1] See, for example, W. T. Richards, Revs. Modern Phys. **11**, 36 (1939).

[2] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, London, 1954), p. 341.

[3] R. E. Peierls, *Quantum Theory of Solids* (Oxford University Press, London, 1955), p. 40.

[4] L. Landau and L. Rumer, Physik Z. Sowjetunion **11**, 18 (1937).

CALCULATION OF THE RATE OF TRANSITION

Oscillator Coupling

The coupling of lattice vibrations with internal oscillations is associated with the nature of intermolecular forces. For example, if these were Hooke's law forces, lattice vibrations would be strictly harmonic and no coupling could result. The actual intermolecular binding forces in molecular crystals are van der Waals' forces which depart considerably from Hooke's law. A good approximation for molecular crystals is given by the Lennard-Jones potential, a function having wide application in the liquid and gaseous state. The binding energy is thus taken to be

$$U(r)=-4\epsilon[(r_0/r)^6-(r_0/r)^{12}]. \tag{2}$$

The above potential is for two molecules with no neighbors. The effect of adding additional neighbors in the crystal lattice is readily deduced in the following elementary argument: The potential of a single molecule with two nearest neighbors all in line at spacing, d, is simply the summation of two pairs: $W(r)=U(r)+U(2d-r)$; transforming in terms of a small displacement from equilibrium, ζ, this potential becomes

$$W=W_0+U_{r=d}''\zeta^2+U_{r=d}^{\mathrm{IV}}\zeta^4/12+\cdots.$$

The cubic term vanishes since W is even. The potential for displacement perpendicular to the molecular line is

$$\Delta W=U'\zeta^2/d+U''\zeta^4/4d^2+\cdots.$$

Hence a three-dimensional, simple cubic lattice of six nearest neighbors with spacing, d, has the potential

$$\Delta W=(U''+2U'/d)\zeta^2+(U^{\mathrm{IV}}/12+U''/2d^2)\zeta^4+\cdots. \tag{3}$$

The first term in each of the brackets corresponds to displacement along the trimolecular line; the second term is the transverse oscillation, involving two pairs of neighbors. Because of symmetry, this expression remains approximately valid for any direction. Anharmonicity results from quartic and higher even-power terms in ζ, and hence these are the important terms which lead to coupling.

Coupling becomes analytically more amenable when transformed to normal coordinates. Following the usual procedure, the coordinate ζ is transformed to a principal coordinate in which the significant motion separates into motion of the center of the molecular mass and motion of the atoms, $\zeta=X+x$, where X is the molecular, and x, the atomic coordinate. The anharmonic coupling potential (neglecting higher than quartic terms) is then

$$H'=A(X+x)^4\simeq 4AX^3x, \tag{4}$$

where

$$A=U^{\mathrm{IV}}/12+U''/2d^2.$$

The omitted terms in the above expansion are insignificant inasmuch as the atomic displacement is certainly small compared to the lattice motion. This expression for the coupling energy obviously represents a considerable idealization for a three-dimensional lattice will, in general, have different elastic constants for different crystal directions. Furthermore, the coordinates X and x are in general not collinear, and some correction factor between $\frac{1}{2}$ and unity should be included. In spite of these approximations the results indicate that the accuracy of the calculation is adequate for the present; the predicted acoustical absorption is a large effect, and absorption measurements are rarely precise.

Transition Probability

Although the calculation of the relaxation time between the two oscillators may be considered a classical one solvable by the usual procedures of classical mechanics, the procedures of quantum mechanics more readily lend themselves to this calculation. For example, in quantum mechanics the transition probability per unit time is a familiar perturbation calculation, given in the form[5]

$$\kappa=t^{-1}\int aa^*\rho(k)dE_k, \tag{5}$$

where

$$a(t)=(i\hbar)^{-1}\int_{-\infty}^{t}H_{01}'\exp(2\pi i\nu_{01}t)dt.$$

As interpreted here, the internal oscillators make transitions between the two quantum states, 0 and 1; the frequency associated with this transition is ν_{01}. Neglect of transitions to higher states corresponds classically to neglect of higher powers of x in Eq. (4) above. The quantity H_{01}' is the matrix element of the transition defined by $H_{01}'=\int\psi_0H'\psi_1dx$ where ψ_0 and ψ_1 are the simple harmonic oscillator wave functions for the states 0 and 1. Utilizing the expression for the coupling potential H' from Eq. (4), the quantity a becomes

$$a=4AX_0^3(i\hbar)^{-1}\int_{-\infty}^{\infty}\psi_0\psi_1xdx\int_{-\infty}^{t}\sin^3(2\pi\nu t)\times\exp(2\pi i\nu_{01}t)dt, \tag{6}$$

where X is considered a classical dynamical variable of the form $X=X_0\sin(2\pi\nu t)$. The integration with respect to time leads to

$$a=\frac{AX_0^3}{2i\hbar}\left[\frac{1-\exp(2\pi it)(3\nu+\nu_{01})}{3\nu+\nu_{01}}+\frac{1-\exp(2\pi it)(\nu_{01}-3\nu)}{\nu_{01}-3\nu}+\frac{1-\exp(2\pi it)(\nu+\nu_{01})}{\nu+\nu_{01}}+\frac{1-\exp(2\pi it)(\nu-\nu_{01})}{\nu-\nu_{01}}\right]\int_{-\infty}^{\infty}\psi_0\psi_1xdx. \tag{7}$$

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[5] For example, see L. Schiff, *Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1949), Sec. 29.

Of the four terms in this equation only the second and fourth are important, and these only if $\nu_{01} \simeq \nu$ and/or $\nu_{01} \simeq 3\nu$. Thus the rather unusual situation obtains with resonance occurring whenever a single quantum of the internal frequency exchanges with either 1 or 3 quanta of the lattice frequency. If each of the molecular coordinates, X, in the coupling potential had been considered independent ($X_1X_2X_3$ instead of X^3), then the resonance would have been restricted to the three quanta exchange, $\nu_{01} \simeq 3\nu$. Actually in all molecules for which data exists, ν_{01} is much larger than the maximum ν, and normal resonance, $\nu_{01} \simeq \nu$, is probably unimportant even if the coordinates X are not independent. This unusual resonance phenomenon may also be described alternatively in terms of phonon collisions; in this case collisions between three lattice phonons and a single internal phonon are required in order that energy and momentum shall be conserved.[3,6]

The remaining integration (with respect to the coordinate x) leads to[7]

$$aa^* = \frac{A^2X_0^6 \sin^2[\pi i(\nu_{01}-3\nu)t]}{4h^2\alpha(\nu_{01}-3\nu)^2}. \tag{8}$$

As ordinarily interpreted, Eq. (5) implies resonance with any *single* upper state for effecting transition. In that case, the quantity $\rho(k)dE_k$ in Eq. (5) is ordinarily defined so that it represents the fraction of lattice states taken *singly* (or single lattice phonons) with energy lying between E_k and E_k+dE_k. However, the above discussion demonstrates that three lattice states (or three lattice phonons) are necessary to effect transition. The distribution function of lattice states, taken in sets of three in the energy range dE_k, is then $[\rho(k)dE_k]^3$. The modified form of Eq. (5) for this case then becomes

$$\kappa = t^{-1}\int\int\int aa^*[\rho(k)dE_k]^3$$
$$= \frac{A^2X_0^6}{4h^2\alpha t}\int\int\int \frac{\sin^2[\pi i(\nu_{01}-3\nu)t]\rho^3(k)dE_k{}^3}{(\nu_{01}-3\nu)^2}. \tag{9}$$

The value of the single integral involving the sine function is small except in the region of resonance so that its integration limits can be extended from $-\infty$ to $+\infty$, a familiar definite integral. Integrating once, yields

$$\kappa = (\pi^2A^2X_0^6h/12\alpha)\int\int \rho^3(k)d\nu^2, \tag{10}$$

which leaves only the problem of evaluating the energy density, $\rho(k)$.

In the Debye theory of specific heats, the distribution of lattice vibrations is taken to be $dN = (3/\nu_m{}^3)\nu^2 d\nu = \rho(k)dE_k$ or $\rho(k) = 3\nu^2/h\nu_m{}^3$, where the parameter ν_m is the maximum lattice frequency as interpreted by Debye. The limits of the remaining integrals above are therefore taken from 0 to ν_m. Hence, the final result obtains:

$$\kappa = \frac{9A^2(kT)^3N^4}{16h\nu_{01}m_{01}\nu_m{}^7(4\pi^2M)^3}, \tag{11}$$

where X_0 has been replaced by its classical value $X_0 = (kT/4\pi^2M\nu^2)^{\frac{1}{2}}$; the molecular weight is M, and N is Avogadro's number.

It will be noted that this result is sensitive to two parameters: the quantity A, determined from the Lennard-Jones potential constants, a measure of the strength of the intermolecular binding forces; the parameter ν_m, interpreted in the original Debye theory as a lattice vibration. If ν_m is truly related to lattice vibrations, it might be expected that it is not independent of the parameter A. However this interpretation remains speculative, and ν_m can best be considered an empirical parameter determined from specific heat data. Although Planck's constant h appears explicitly, the calculation is not dependent fundamentally upon quantum mechanics; it will be noted that the product $h\nu_{01}$ occurs in the denominator corresponding classically to the energy of the internal oscillator.

AN ILLUSTRATIVE EXAMPLE: BENZENE

A small value for the transition probability, κ, leads to large acoustic absorption. Hence, the phenomenon of resonance absorption should be most readily observable in substances for which Eq. (11) leads to a small value. Such substances might in general be expected to be characterized by (1) a relatively large molecular weight, (2) a large fundamental vibrational frequency, and (3) a large Debye frequency. However, these first two characteristics are in general in opposition and their combined effect may not be relatively important. Probably of considerable importance is the requirement that A is small, or the binding forces weak; this implies that the Lennard-Jones parameters ϵ and r_0, are small and the intermolecular spacing large.

An illustrative example, benzene, was selected for study. This substance is almost the ideal molecular crystal. Simpler molecules exist, but benzene is probably the simplest molecular substance existing in the solid state which can be studied over the wide temperature range necessary to establish accurate specific heat data; no complications arise out of polymorphic transitions, molecular disorder, or hydrogen bonding. Raman and infrared spectra have been studied extensively as well as intermolecular potentials leading to the Lennard-Jones parameters.

The values for benzene for evaluation of the transition probability are given in Table I. Substitution in Eq.

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[6] E. Bauer, J. Chem. Phys. **26**, 1440 (1957).

[7] The simple harmonic oscillator wave functions are

$$\psi_0 = (\alpha/\pi)^{\frac{1}{4}} \exp(-\alpha x^2/2),$$
$$\psi_1 = (\alpha/\pi)^{\frac{1}{4}} 2(\alpha)^{\frac{1}{2}} x \exp(-\alpha x^2/2),$$

where $\alpha = 4\pi^2 m_{01}\nu_{01}/h$.

(11) leads to $\kappa = 10^9/\text{sec}$; this is rather a low value compared to transition probabilities in other processes. The predicted acoustic absorption utilizing Eq. (1) together with this transition probability is about 0.5 cm^{-1} at 10^7 cps; resonance absorption will vary as the square of the frequency. Hence absorption arising from resonance is orders of magnitude greater than has thus far been observed in crystals (e.g., quartz, metals).

In order to test this prediction, a large single crystal of benzene of linear dimensions about 7 cm was grown from the purified liquid and its acoustic absorption measured. The details of the method of crystal growth and acoustic measurement are to be published elsewhere.[8] The measured absorption of longitudinal acoustic waves at 10^7 cps was found to be 0.24 cm^{-1}. At frequencies around 6.4×10^6 cps the absorption was 0.09 cm^{-1}. In the frequency range measured, the frequency dependence was proportional to ω^2 as predicted. As a check on the experiment, measurements on a sample of ice obtained from a block of commercial ice of rather poor optical quality yielded 0.04 cm^{-1} at 10^7 cps. In view of the many approximations inherent in the theory, this agreement between observation and theory is considered adequate.

TABLE I. Numerical constants for benzene.

ϵ (Lennard-Jones parameters)[a]	6.15×10^{-6} erg
r_0	5.27×10^{-8} cm
d (intermolecular spacing)[b]	5.03×10^{-8} cm
$A(\epsilon, r_0, d)$ (coupling parameter)	1.73×10^{20} g cm^6/sec^2
ν_m (Debye frequency)[c]	3.1×10^{12} sec^{-1}
ν_{01} (internal vibrational frequency)[d]	1.21×10^{13} sec^{-1}
M (molecular weight)	78.11 g
m_{01} (apparent internal vibrating mass)[d]	24 g
T (temperature)	273°K

[a] Hirschfelder, Curtis, and Bird, *Molecular Theory of Gases and Liquids* (John Wiley and Sons, Inc., New York, 1954), p. 1112.
[b] E. R. Andrew and R. G. Eades, Proc. Roy. Soc. (London) **A218**, 537 (1953).
[c] Lord, Ahlberg, and Andrews, J. Chem. Phys. **5**, 649 (1937).
[d] R. C. Lord, Jr., and D. H. Andrews, J. Phys. Chem. **41**, 149 (1937).

DISCUSSION

The above calculation is capable of considerable refinement. The crystal symmetry of benzene is not simple cubic, as assumed, but simple orthorhombic (*Pbca*); nor does a single acoustic wave propagate, but longitudinal and transverse waves may exist, each with characteristic elastic constants in the three crystallographic axes. Further, the Lennard-Jones potential is a central force field intended for spherically symmetric molecules; in addition the constants used were determined from the vapor rather than the crystalline state. In spite of these obvious simplifications, the immediate result is meaningful. The predicted and observed absorption is orders of magnitude higher than has been observed in other crystalline substances (in which resonance absorption is believed to be negligible). The major source of acoustic dissipation in solid benzene, and undoubtedly in many other substances, is certainly resonance absorption.

It would be of interest to search for additional examples of resonance absorption in molecular crystals. Tabular values of Lennard-Jones coefficients for other molecules indicate that the coupling coefficient A is comparable to that in benzene in a number of other simple organic substances. With the aid of a more precise theory, measurements of acoustic absorption may well yield significant molecular properties.

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[8] L. Liebermann, J. Acoust. Soc. Am. (to be published).