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ABSORPTION OF ULTRASOUND IN ORGANIC CRYSTALS

Denis F. Strenzwilk
Peter D. Yedinak

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USA BALLISTIC RESEARCH LABORATORIES
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In this paper we present our expression for the transition rate for a molecule in an organic crystal to absorb three phonons of lattice energy into the lowest frequency molecular vibrational mode ($0 \rightarrow 1$ transition). Our model is a three dimensional simple cubic lattice with nearest neighbor central and noncentral forces between molecules situated at the lattice sites. After making some approximations, we compare our expression with the transition rate determined from ultrasonic experiments on benzene, p-dichlorobenzene, carbon

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tetrachloride, and cyclohexane, and discuss the results. We also point out the improvement our expression offers over the transition rate derived by Liebermann and used by other investigators.

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PREFACE

The Army is interested in understanding the nature of molecular crystals of explosives and propellants. The long-term objectives of this research are:

1. capability to predict the intrinsic sensitivity to the initiation of chemical reactions,

2. capability to predict the essential physical properties needed by new organic compounds to be useful as explosives or propellants.

There is a general feeling that the advances in knowledge of microscopic properties of matter, discovered in physics and chemistry over the last 30 years, could be profitably applied to this problem. This research would furnish information that cannot be obtained by the more usual continuum hydrodynamic approach. It is clear that several steps are involved between the introduction of energy into a solid and the eventual chemical reactions which result. One area in which microscopic modeling should yield useful results is the study of energy transfer through the crystal and the accumulation of that energy in a particular molecule. It is obvious that such steps must precede the dissociation of the molecule and the formation of a new species.

The approach of our work is to bring together many well established ideas from several branches of physics and chemistry, making the minimal adjustments necessary to use them on molecular crystals of explosives and propellants. Then, we use these ideas to describe coherently the process whereby ultrasonic energy in a solid is absorbed into a particular molecule. Specifically we look at the phenomenon of resonance absorption - that is, the process of energy transfer between the lattice vibrations of the solid and the lowest internal vibrational mode of the molecules which make up the solid. We feel that the understanding of chemical reactions caused by shock or thermal initiation, as well as models for microscopic 'hot spots' caused by defects, will be improved by the study of resonance absorption.

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LIST OF SYMBOLS

a	the ratio Ω/ω_o
$a_{\bar{k}j}$	annihilation operator for phonons whose wavevector is $\bar{k}$ and which belong to the jth branch
$a^{+}_{\bar{k}j}$	creation operator for phonons whose wavevector is $\bar{k}$ and which belong to the jth branch
A_x	amplitude of normal mode in x direction defined in Equation (10a)
a_1,a_2,a_3	integers defined in Equation (10c)
b_L	annihilation operator for the lowest vibrational mode of the Lth molecule
b^{+}_L	creation operator for the lowest vibrational mode of the Lth molecule
B_n	Bernoulli numbers
C	constant defined in Equation (35a)
c_n or $c_n(a)$	coefficient of the nth power of α in Equation (44), which is a function of the constant a
C_p	specific heat per mole at constant pressure
C_v	specific heat per mole at constant volume
C'	specific heat per mole associated with that part of molecular energy which relaxes
d	equilibrium lattice separation
$\bar{e}\binom{\bar{k}}{j}$	vector defined in Equation (12)
E_o	eigenvalue of H_o defined in Equation (24)
$f_n(x,y)$	defined in Table I of Appendix A
f_{01}	transition rate for the molecule to go from 0 → 1, defined in Equation (51)
f_{10}	transition rate for the molecule to go from 1 → 0, defined in Equation (50)

$g(x)$	dimensionless density of states function defined in Equation (35f)
$g(\omega_j(\bar{k}))$	density of states per frequency
$\hbar$	Planck's constant divided by 2π
H_{int}	interaction Hamiltonian defined in Equation (6)
H_{lat}	Hamiltonian for lattice dynamical energy defined in Equation (7)
H_{mol}	Hamiltonian for the total vibrational energy defined in Equation (18)
H_o	Hamiltonian which is the sum of H_{lat} and H_{mol} defined in Equation (21)
H_{tot}	Hamiltonian which is the sum of H_o and H_{int} defined in Equation (26)
$\hat{i}$	unit vector in x direction
$I(a,\alpha)$	integral defined in Equation (42)
j	integer index for the jth branch
$\hat{j}$	unit vector in y direction
$\bar{k}$	wavevector defined in Equation (13)
$\hat{k}$	unit vector in z direction
k_B	Boltzmann's constant
(ℓ, m, n)	integers denoting the equilibrium position of the Lth molecule
M	mass of a molecule
$n\begin{pmatrix}\bar{k}\\ j\end{pmatrix}$	phonon occupation number corresponding to the jth branch of the mode with wavevector $\bar{k}$
$\langle n\begin{pmatrix}\bar{k}_i\\ j\end{pmatrix}\rangle$	Planck distribution defined in Equation (31)
$n(L)$	molecular-vibrational quantum number for the Lth molecule
N	number of molecules in the X,Y, or Z direction for which periodic boundary conditions hold

p	equal to α-2, defined in Equation (46)
P_{if}	probability of going from the initial state $\vert i\rangle$ to the final state $\vert f\rangle$, defined in Equation (27)
$Q_j(a_1,a_2,a_3)$	same as $Q\begin{pmatrix}\bar{k}\\ j\end{pmatrix}$
$Q\begin{pmatrix}\bar{k}\\ j\end{pmatrix}$	the complex mass weighted normal coordinate for the jth branch of the mode with wavevector $\bar{k}$
R	transition rate which gives the total transition probability per unit time that the system initially in the state $\vert i\rangle$ is in any of the many final states $\vert f\rangle$. It is defined in Equation (41) for the $0 \rightarrow 1$ molecular transition
R_{expt}	experimental value of the transition rate defined in Equation (52)
$\bar{R}_L$	vector denoting the equilibrium position of the Lth molecule
T	temperature in degrees Kelvin
t	time
$u(\ell,m,n)$	phase factor defined in Equation (10b)
$u_k(\ell,m,n)$	phase factor defined in Equation (10b) for wavevector $\bar{k}$
$U(X,Y,Z)$	potential energy of the Lth molecule with its six nearest neighbors held fixed, defined in Equation (1)
V	velocity of sound
$v(L)$	same as $v_{\ell mn}$
$v_{\ell mn}$	normal coordinate for the molecular vibrational mode of the Lth molecule
x	dimensionless dummy variable defined in Equation (35d)
X	displacement coordinate of the center-of-mass from equilibrium in x-direction
$x_{\ell mn}$	redefined displacement coordinates in x-direction of the center-of-mass of the Lth molecule from the (ℓ,m,n) equilibrium position
y	dimensionless dummy variable defined in Equation (35d)

Y	displacement coordinate of the center-of-mass from equilibrium in the y-direction
$y_{\ell mn}$	redefined displacement coordinates in the y-direction of the center-of-mass of the Lth molecule from the (ℓ,m,n) equilibrium position
z	dimensionless dummy variable defined in Equation (35d)
Z	displacement coordinate of the center-of-mass from equilibrium in the z-direction
$z_{\ell mn}$	redefined displacement coordinates in the z-direction of the center-of-mass of the Lth molecule from the (ℓ,m,n) equilibrium position
α	equals $\hbar\omega_o/k_BT$
β	absorption coefficient defined in Equation (48) and Equation (49)
γ_c	central force constant in Equation (7)
γ_{nc}	noncentral force constant in Equation (7)
δ	Dirac delta function
η	the Lennard-Jones parameter for the maximum energy of attraction of the two molecules
θ	equals $\hbar\omega_o/k_B$
λ_1	proportional to the second derivative of U(X,Y,Z) evaluated at (0,0,0) defined in Equation (3a)
λ_2	proportional to the fourth derivative of U(X,Y,Z) evaluated at (0,0,0) defined in Equation (3b)
λ_3	proportional to the fourth derivative of U(X,Y,Z) evaluated at (0,0,0) defined in Equation (3c)
μ_L	reduced mass of Lth molecule
ν	frequency of the sound wave in Table 6
ν_D	Debye frequency
ν_o	maximum lattice frequency
σ	the Lennard-Jones parameter for the distance of closest approach of two molecules which collide with zero initial relative kinetic energy

τ	relaxation time equal to $1/f_{10}$
ϕ_j	defined in Equation (10c)
$\|\Psi\rangle$	eigenfunction of H_o defined in Equation (23)
Ω	circular frequency for the lowest vibrational mode of the Lth molecule
ω	circular frequency of the sound wave in Equation (48) and Equation (49)
ω_D	Debye circular frequency defined in Equation (28b)
$\omega_j(\bar{k})$	circular frequency for the jth branch of the mode with wavevector $\bar{k}$, defined in Equation (14)
ω_o	maximum circular lattice frequency defined in Equation (15)

I. INTRODUCTION

Originally, we became interested in studying the way that lattice vibrational (phonon) energy is absorbed into the molecular-vibrational mode of a defect molecule or a molecule located next to a defect. In these organic crystals the forces between the atoms in a molecule are much stronger than the van der Waals - type forces between molecules in the crystal. The energy necessary to excite the $0 \rightarrow 1$ transition in the lowest-frequency mode of a molecular vibration is usually much higher than the energy of the highest-frequency phonon in a perfect crystal. Thus, a multiphonon process is usually required to excite a molecular vibration. During the course of our literature search for our previous paper[1], we found some papers by Liebermann[2-4] which coupled the lattice vibrations to the molecular vibrations in perfect crystals in essentially a standard way and suggested that the ultrasonic absorption observed in benzene could be explained by this coupling. Other investigators[5-9] have subsequently observed ultrasonic absorption in other crystals and used Liebermann's model to analyze their results. As the agreement between theory and experiment left some doubt as to whether or not Liebermann's model adequately explained the phenomenon called 'resonance absorption', we began to inspect his model very carefully. We have discovered that Liebermann made an unfortunate error in carrying out the details of his model, which invalidates his final theoretical expression for the transition rate for lattice energy to be absorbed into the molecule. As this expression is still being used by the other investigators, we have decided to formulate a model, similar to the one of Liebermann, and calculate an expression for the transition rate. Our new result can be assessed by the previous investigators on their experimental work, and the direction of future research on this phenomenon can be suggested from such studies.

In our model we consider a simple cubic lattice composed of molecules separated by a constant lattice spacing. We make the approximation that the center-of-mass motion of each molecule is nearly independent of the motion of the atoms with respect to the center of mass.

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1. D.F. Strenzwilk and P.D. Yedinak, Phys. Rev. 7, 874 (1973).
2. L. Liebermann, Phys. Rev. 113, 1052 (1959).
3. L. Liebermann, J. Acoust. Soc, Am. 31, 1073 (1959).
4. L. Liebermann,"Physical Acoustics", Vol. IV, Part A (Acad. Press,NY, 1966) ed. by W.P. Mason, p. 183.
5. R.A. Rasmussen, J. Chem. Phys. 36, 1821 (1962).
6. S.S. Yun, and R.T. Beyer, J. Chem. Phys. 40, 2538 (1964).
7. J.D. Wilson, and S.S. Yun, J. Acoust. Soc. Am. 50, 164 (1971).
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9. A.E. Victor, and R.T. Beyer, J. Acoust. Soc. Am. 54, 1639 (1973).

Then the term which couples the two motions contains the only anharmonic factors in our model. The center-of-mass motion is treated in the same manner as a monatomic simple cubic lattice in which the nearest neighbors interact through a central force derivable from a Lennard-Jones "6-12" potential and a non-central force which we have arbitrarily made consistent with the Debye frequency. The molecular vibrations are assumed to be the same as in the gas phase. Using a modified Debye distribution for the lattice frequencies and the Planck distribution for the occupation numbers of the various modes, we have calculated the transition rate for a molecule to absorb energy from the lattice.

II. THEORY

A. Coupling Term.

Consider the Lth molecule in a simple cubic crystal with its six nearest neighbors at equilibrium lattice separation, d, and assume a Lennard-Jones "6-12" potential between molecules. If the center of mass of Lth molecule, whose equilibrium position is denoted by $\bar{R}_L = d(\ell\hat{i} + m\hat{j} + n\hat{k})$, is moved a small distance (X,Y,Z), while the nearest neighbor molecules are held fixed, (as the other investigators[2-8] have done for simplicity), we can write the potential energy for the Lth molecule in terms of the molecule located at (0,0,0) without loss of generality as follows,

$$U(X,Y,Z) = 4\eta\sum_{\ell mn}\left\{\frac{\sigma^{12}}{\left[(X-\ell d)^2 + (Y-md)^2 + (Z-nd)^2\right]^6} - \frac{\sigma^6}{\left[(X-\ell d)^2 + (Y-md)^2 + (Z-nd)^2\right]^3}\right\} \tag{1}$$

where η and σ are constants depending of the kind of molecules involved, and $\ell^2 + m^2 + n^2 = 1$, and $\ell, m, n = 0, 1, -1$.

If we expand this potential in a Taylor series to the fourth order about the origin (0,0,0) in X,Y,Z, we obtain:

$$U(X,Y,Z) = U(0,0,0) + \lambda_1(X^2 + Y^2 + Z^2) + \lambda_2(X^4 + Y^4 + Z^4) + \lambda_3(X^2Y^2 + X^2Z^2 + Y^2Z^2) + \ldots, \tag{2}$$

where

$$\lambda_1 \equiv \frac{1}{2} \left. \frac{\partial^2 U}{\partial x_i^2} \right|_{(0,0,0)} = \eta \left[\frac{528\sigma^{12}}{d^{14}} - \frac{120\sigma^6}{d^8} \right] , \tag{3a}$$

$$(x_1, x_2, x_3) \equiv (X,Y,Z), \qquad i,j = 1,2,3, \qquad i \neq j$$

$$\lambda_2 \equiv \frac{1}{24} \left. \frac{\partial^4 U}{\partial x_i^4} \right|_{(0,0,0)} = \eta \left[\frac{11256\sigma^{12}}{d^{16}} - \frac{1104\sigma^6}{d^{10}} \right] , \tag{3b}$$

and

$$\lambda_3 \equiv \frac{1}{4} \left. \frac{\partial^4 U}{\partial x_i^2 \partial x_j^2} \right|_{(0,0,0)} = \eta \left[\frac{-9744\sigma^{12}}{d^{16}} + \frac{1632\sigma^6}{d^{10}} \right] . \tag{3c}$$

It should be noted that the third derivative vanishes since the potential is an even function. To estimate the coupling between the lattice and molecular vibration, we assume that

$$X = x_{\ell mn} + \frac{v_{\ell mn}}{\sqrt{3}} , \tag{4a}$$

$$Y = y_{\ell mn} + \frac{v_{\ell mn}}{\sqrt{3}} , \tag{4b}$$

and

$$Z = z_{\ell mn} + \frac{v_{\ell mn}}{\sqrt{3}} . \tag{4c}$$

where

$x_{\ell mn}, y_{\ell mn}, z_{\ell mn}$ - redefined displacement coordinates about the Lth equilibrium position $\bar{R}_L = d(\ell \hat{i} + m\hat{j} + n\hat{k})$ for the center-of-mass of the molecule.

$v_{\ell mn}$ - normal coordinate for the molecular vibrational mode of Lth molecule.

This is an approximation since the exact treatment would break up the motion of each atom in a molecule into motion of the center of mass of the molecule and motion with respect to the center of mass. It would also have to take into account the forces between atoms in different molecules and not just the average intermolecular force between centers. An example of a more rigorous treatment of this coupling can be found in Rasmussen's[5] earlier paper on solid cyclohexane, but in a later paper[8] on carbon tetrachloride he used the simpler form of Liebermann. We also assume that the amplitude of the center of mass is much greater than the molecular-vibrational coordinate, i.e.,

$$\left| x_{\ell mn} \right|_{max}, \left| y_{\ell mn} \right|_{max}, \left| z_{\ell mn} \right|_{max} \gg \left| v_{\ell mn} \right|_{max} . \qquad (5)$$

If we substitute Eq. (4) in Eq. (2), neglecting not only terms which do not mix the coordinates x,y,z, and v since they contribute to the uncoupled energy, but also terms involving $x^2v^2,\ldots,$ and $xv^3,\ldots$ because of Eq. (5), we have the coupling between the lattice and molecular vibrations, viz.,

$$\begin{aligned} H_{int} \approx {} & \frac{2}{\sqrt{3}} \lambda_1 v_{\ell mn} (x_{\ell mn} + y_{\ell mn} + z_{\ell mn}) + \frac{4}{\sqrt{3}} \lambda_2 v_{\ell mn} (x^3_{\ell mn} + y^3_{\ell mn} + z^3_{\ell mn}) \\ & + \frac{2}{\sqrt{3}} \lambda_3 v_{\ell mn} (x_{\ell mn} y^2_{\ell mn} + y_{\ell mn} x^2_{\ell mn} + x_{\ell mn} z^2_{\ell mn} + z_{\ell mn} x^2_{\ell mn} \qquad (6) \\ & + y_{\ell mn} z^2_{\ell mn} + z_{\ell mn} y^2_{\ell mn}) , \end{aligned}$$

where the interaction Hamiltonian or coupling term is H_{int}.

B. Total Energy of Crystal

The main contribution to the energy of this system is composed of the lattice dynamical energy of the molecules as a whole, and the energy of the molecular vibrations. For the lattice energy in the harmonic approximation, we have chosen the model of Montroll-Potts-Rosenstock-Newell (MPRN)[10,11] where the lattice coordinates (x,y,z) appear quadratically in the potential energy. The Hamiltonian for the lattice, H_{lat}, is

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[10] E.W. Montroll, and R.B. Potts, Phys. Rev. 100, 525 (1955).

[11] H.B. Rosenstock and G.F. Newell, J. Chem. Phys. 21, 1607 (1953).

$$
\begin{aligned}
H_{lat} = {} & \tfrac{1}{2} M \sum_{\ell mn} (\dot{x}^2_{\ell mn}+\dot{y}^2_{\ell mn}+\dot{z}^2_{\ell mn}) + \tfrac{1}{2} \gamma_c \sum_{\ell mn} [(x_{\ell mn}-x_{\ell +1,mn})^2 \\
& + (y_{\ell mn}-y_{\ell ,m+1,n})^2 + (z_{\ell mn}-z_{\ell m\, n+1})^2] \\
& + \tfrac{1}{2} \gamma_{nc} \sum_{\ell mn} [(x_{\ell mn}-x_{\ell ,m+1,n})^2 \\
& + (y_{\ell mn}-y_{\ell m,n+1})^2 + (z_{\ell mn}-z_{\ell +1,mn})^2 + (x_{\ell mn}-x_{\ell m,n+1})^2 \\
& + (y_{\ell mn}-y_{\ell +1,mn})^2 + (z_{\ell mn}-z_{\ell ,m+1,n})^2] \quad ,
\end{aligned}
\tag{7}
$$

where M is the mass of a molecule, $\gamma_c \equiv 2\lambda_1$ is the central force constant and γ_{nc} is the noncentral force constant.

For a perfect lattice composed of identical molecules of mass M, the equations of motion for a system composed of $N \times N \times N = N^3$ particles with nearest-neighbor central and noncentral interactions only are

$$
\begin{aligned}
M \ddot{x}_{mn} = {} & \gamma_c (x_{\ell +1,mn}-2x_{\ell mn}+x_{\ell -1,mn}) + \gamma_{nc}(x_{\ell ,m+1,n}-2x_{\ell mn}+x_{\ell ,m-1,n}) \\
& + \gamma_{nc}(x_{\ell m,n+1}-2x_{\ell mn}+x_{\ell m,n-1}) \quad ,
\end{aligned}
\tag{8a}
$$

$$
\begin{aligned}
M \ddot{y}_{mn} = {} & \gamma_c (y_{\ell ,m+1,n}-2y_{\ell mn}+y_{\ell ,m-1,n}) + \gamma_{nc}(y_{\ell m,n+1}-2y_{\ell mn}+y_{\ell m,n-1}) \\
& + \gamma_{nc}(y_{\ell +1,mn}-2y_{\ell mn}+y_{\ell -1,mn}) \quad ,
\end{aligned}
\tag{8b}
$$

and

$$
\begin{aligned}
M \ddot{z}_{mn} = {} & \gamma_c (z_{\ell m,n+1}-2z_{\ell mn}+z_{\ell m,n-1}) + \gamma_{nc}(z_{\ell +1,mn}-2z_{\ell mn}+z_{\ell -1,mn}) \\
& + \gamma_{nc}(z_{\ell ,m+1,n}-2z_{\ell mn}+z_{\ell ,m-1,n}) \quad ,
\end{aligned}
\tag{8c}
$$

$$\ell ,m,n = -\frac{1}{2} N + 1, \ldots , \frac{1}{2} N , \qquad N_{even} ,$$

where we assume periodic boundary conditions:

$$x_{\ell mn} = x_{\ell +N,mn} = x_{\ell ,m+N,n} = x_{\ell m,n+N} , \text{ etc.} \tag{9}$$

The normal modes for Eq. (8a) can be expressed in terms of the amplitude A_x as

$$x_{\ell mn} = A_x \, u(\ell mn) \exp(-i\omega t) \ , \tag{10a}$$

where

$$u(\ell mn) = \exp i(\phi_1 \ell + \phi_2 m + \phi_3 n) \tag{10b}$$

and for j = 1,2,3

$$\phi_j = (2\pi a_j / N); \ a_1, a_2, a_3 = 1,2,\ldots,N \tag{10c}$$

or $-\frac{1}{2}N+1,\ldots,\frac{1}{2}N$.

Similar solutions satisfy Eqs. (8b) and (8c).

The general solution[12] is given by the following expansion in terms of plane waves:

$$x_{\ell mn} = \frac{1}{(N^3 M)^{\frac{1}{2}}} \sum_{\substack{a_1,a_2,a_3=1 \\ j=1,2,3}}^{N} e_x \begin{pmatrix} \bar{k} \\ j \end{pmatrix} Q_j(a_1,a_2,a_3) \, u_k(\ell mn) \ , \tag{11}$$

where $Q_j(a_1,a_2,a_3,) \equiv Q \begin{pmatrix} \bar{k} \\ j \end{pmatrix}$ is the complex, mass-weighted, normal coordinate for the jth branch of the mode with wavevector $\bar{k}$, $e_x \begin{pmatrix} \bar{k} \\ j \end{pmatrix}$ is the x-component of the vector $\bar{e} \begin{pmatrix} \bar{k} \\ j \end{pmatrix}$ with the definition in the MPRN model

$$\bar{e} \begin{pmatrix} \bar{k} \\ 1 \end{pmatrix} = (1,0,0); \ \bar{e} \begin{pmatrix} \bar{k} \\ 2 \end{pmatrix} = (0,1,0); \ \bar{e} \begin{pmatrix} \bar{k} \\ 3 \end{pmatrix} = (0,0,1) \ , \tag{12}$$

and wavevector $\bar{k}$ is

$$\bar{k} = \frac{2\pi}{Nd} (a_1 \hat{i} + a_2 \hat{j} + a_3 \hat{k}) \ . \tag{13}$$

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[12] A.A. Maradudin, E.W. Montroll, and G.H. Weiss, "Solid State Physics", supp. 3, (Acad. Press, NY, 1963).

The y and z displacements have similar expansions. Corresponding to each mode $\begin{pmatrix}\bar{k}\\ j\end{pmatrix}$ is a circular frequency which satisfies

$$M\,\omega_j^2(\,\bar{k}\,) = 2\sum_{i=1}^{3}\gamma_i\,(1-\cos\phi_i)\ , \tag{14}$$

where $\gamma_j \equiv \gamma_c$ and $\underset{i\neq j}{\gamma_i} \equiv \gamma_{nc}$.

The maximum lattice frequency ω_o is

$$\omega_o^2 = 4\,\frac{(\gamma_c + 2\,\gamma_{nc})}{M}\quad . \tag{15}$$

C. Quantum Mechanics

The energy of the lattice in Eq. (7) can be quantized by expressing $Q\begin{pmatrix}\bar{k}\\ j\end{pmatrix}$ by the following transformation which can be found in standard texts^{12}:

$$Q\begin{pmatrix}\bar{k}\\ j\end{pmatrix} = \left(\frac{\hbar}{2\omega_j(\bar{k})}\right)^{1/2}\left(a^{+}_{-\bar{k}j} + a_{\bar{k}j}\right)\ , \tag{16a}$$

and

$$\dot{Q}\begin{pmatrix}\bar{k}\\ j\end{pmatrix} = P\begin{pmatrix}\bar{k}\\ j\end{pmatrix} = i\left(\frac{\hbar\,\omega_j(\bar{k})}{2}\right)^{1/2}\left(a^{+}_{-\bar{k}j} - a_{\bar{k}j}\right)\ , \tag{16b}$$

where $a^{+}_{\bar{k}j}$ and $a_{\bar{k}j}$ are the creation and annihilation operators, respectively, for phonons whose wavevector is $\bar{k}$ and which belong to the jth branch, and $\hbar$ is Planck's constant divided by 2π. These operators obey the usual commutation relations of lattice dynamics and have familiar matrix elements for Bose operators in the numbers representation. Thus, Eq. (7) becomes a sum of quantum-mechanical operators in the numbers representation when Eq. (16) is substituted into either Eq. (11) or the similar expressions for the y and z displacements, i.e.,

$$H_{lat} = \sum_{\substack{\bar{k}\\ j}} \hbar\, \omega_j(\bar{k})\ (a^{+}_{\bar{k}j} a_{\bar{k}j} + 1/2)\ . \qquad (17)$$

The molecular-vibrational energy for the lowest vibrational mode of the Lth molecule in the crystal can be expressed in terms of its reduced mass μ_L, the vibrational frequency Ω, and the normal coordinate for this mode v(L), so that the total vibrational energy can be expressed as

$$H_{mol} = \frac{1}{2} \sum_L (\mu_L\, \dot{v}^2(L) + \Omega^2\, v^2(L)\ )\ , \qquad (18)$$

where H_{mol} is the molecular-vibrational Hamiltonian. This Hamiltonian can be quantized by expressing the normal coordinate v(L) by the following transformations

$$v(L) = \left(\frac{\hbar}{2\mu_L \Omega}\right)^{\frac{1}{2}} (b^{+}_L + b_L)\ , \qquad (19a)$$

and

$$\mu_L\ \dot{v}(L) = p(L) = i\left(\frac{\mu_L \hbar \Omega}{2}\right)^{\frac{1}{2}} (b^{+}_L - b_L)\ , \qquad (19b)$$

where b^{+}_L and b_L are the creation and annihilation operators, respectively. These operators obey the usual commutation relations and have the familiar matrix elements for Bose operators in the numbers representation. Thus, Eq. (18) also becomes a sum of harmonic oscillator operators, one for each molecule, viz.,

$$H_{mol} = \sum_L \hbar\Omega\ (b^{+}_L\, b_L + 1/2)\ . \qquad (20)$$

The total uncoupled energy of the crystal in our model is given by the addition of the lattice energy of Eq. (17) and the molecular-vibrational energy of Eq. (20) to yield the Hamiltonian,

$$H_0 = H_{lat} + H_{mol}\ , \qquad (21)$$

which operates on the eigenket $|\psi\rangle$ that is the product of harmonic oscillator functions in the numbers representation, i.e.,

$$H_0|\psi\rangle = E_0|\psi\rangle , \tag{22}$$

where

$$|\psi\rangle = \left|n(1),n(2),\ldots,n(N^3);\ n\begin{pmatrix}\bar{k}_1\\ 1\end{pmatrix},\ n\begin{pmatrix}\bar{k}_1\\ 2\end{pmatrix},\ n\begin{pmatrix}\bar{k}_1\\ 3\end{pmatrix},\ldots,n\begin{pmatrix}\bar{k}_{N^3}\\ 3\end{pmatrix}\right\rangle, \tag{23}$$

where n(1), n(2), etc. are the molecular-vibrational quantum numbers corresponding to the Lth molecule, and the $n\begin{pmatrix}\bar{k}_i\\ j\end{pmatrix}$ are the phonon occupation numbers corresponding to the lattice vibrational mode designated by the wave vector $\bar{k}_i$ and acoustical branch j. There are no lattice optical branches in the MPRN model.

The eigenvalue E_0 is the sum of $4N^3$ harmonic oscillators, i.e.,

$$E_0 = \sum_{k,j} (n\begin{pmatrix}\bar{k}\\ j\end{pmatrix} + 1/2)\ \hbar\ \omega_j(\bar{k}) + \sum_{L} (n(L) + 1/2)\ \hbar\ \Omega . \tag{24}$$

If we quantize Eq. (6) by the same procedures used for Eq. (17) and Eq. (20), H_{int} becomes

$$\begin{aligned} H_{int} = {} & \frac{2}{\sqrt{3}}\ \lambda_1\ v(L)\ \left[\frac{1}{(N^3M)^{\frac{1}{2}}} \sum_{\bar{k}j} Q\begin{pmatrix}\bar{k}\\ j\end{pmatrix} u_k(\ell mn)\right] \\ & + \frac{4}{\sqrt{3}}\ \lambda_2\ v(L)\ \left[\frac{1}{(N^3M)^{3/2}} \sum_{\substack{kk'k''\\ j}} Q\begin{pmatrix}\bar{k}\\ j\end{pmatrix} Q\begin{pmatrix}\bar{k}'\\ j\end{pmatrix} Q\begin{pmatrix}\bar{k}''\\ j\end{pmatrix} u_k u_{k'} u_{k''}\right] \\ & + \frac{2}{\sqrt{3}}\ \lambda_3\ v(L)\ \left[\frac{1}{(N^3M)^{3/2}} \sum_{\substack{kk'k''\\ j,j'(j\neq j')}} Q\begin{pmatrix}\bar{k}\\ j\end{pmatrix} Q\begin{pmatrix}\bar{k}'\\ j'\end{pmatrix} Q\begin{pmatrix}\bar{k}''\\ j'\end{pmatrix} u_k u_{k'} u_{k''}\right], \end{aligned} \tag{25}$$

where $Q\begin{pmatrix}\bar{k}\\ j\end{pmatrix}$ and v(L) are the operators defined in Eq. (16) and Eq. (19), respectively. Hereafter, the first term in Eq. (25), which can transfer energy only when the phonon frequency equals the molecular vibrational frequency, will be dropped since $\Omega > \omega_0$ in our model.

The total Hamiltonian operator H_{tot} is the sum of Eq. (21) and Eq. (25), i.e.

$$H_{tot} = H_o + H_{int}, \tag{26}$$

where H_{int} contains the only anharmonic terms in this model. It is this interaction Hamiltonian H_{int} which allows the energy to flow from the lattice into a molecule. From time-dependent perturbation theory the probability P_{if} of going from the initial state $|i\rangle$ to the final state $|f\rangle$, when the lattice and ℓth molecule at time $t = 0$ are in a state that exactly corresponds to one of the eigenstates of the unperturbed system $|i\rangle$, is

$$P_{if} = \left(\frac{2\pi}{\hbar^2}\right) t|\langle f|H_{int}|i\rangle|^2 \quad \delta\left(\frac{E_0^f - E_0^i}{\hbar}\right), \tag{27}$$

where the Dirac δ function is used and the superscripts f and i refer to the final and initial states, respectively.

There are many final states $|f\rangle$ in which the system could be after making a transition from the given initial state $|i\rangle$. The density of states per frequency $g(\omega_j(\bar{k}))$ has been worked out for this model by Montroll[10,13]. He showed that the Debye frequency distribution was given as

$$\begin{aligned} g(\omega_j(\bar{k})) &= 3N^3 \; \omega_j^2(\bar{k})/\omega_D^3 \; , && 0 \leqslant \omega_j(\bar{k}) < \omega_D \\ &= 0 && \omega_j(\bar{k}) > \omega_D \end{aligned} \tag{28a}$$

where the circular Debye frequency ω_D, (which is 2π times the Debye frequency ν_D, i.e., $\omega_D=2\pi\nu_D$), equals

$$\omega_D^3 = 6\pi^2\left(\frac{\gamma_c \; \gamma_{nc}^2}{M^3}\right)^{\frac{1}{2}} \quad . \tag{28b}$$

We decided to renormalize the Debye distribution so that the maximum frequency $\omega_o=2\pi\nu_o$ of the MPRN model, which is greater than ω_D, would be included in our frequency spectrum, thus

$$\begin{aligned} g(\omega_j(\bar{k})) &= 3N^3 \; \omega_j^2(\bar{k})/\omega_0^3 \; , && 0 \leqslant \omega_j(\bar{k}) < \omega_0 \\ &= 0 && \omega_j(\bar{k}) > \omega_0 \; . \end{aligned} \tag{29}$$

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[13] E.W. Montroll, in "Third Berkeley Symposium on Mathematical Statistics and Probability", ed. by J. Neyman, (Univ. Cal. Press, Berkeley and Los Angeles, 1956), p. 209.

The purpose of the renormalization was that we wanted to keep the high frequency phonons in our distribution which are truly present, but we did not want to add the additional mathematical difficulty of using the exact density of states which can be found in Montroll's paper. The transition rate R gives the total transition probability per unit time that the system initially in the state $|i\rangle$ is in any of the many final states $|f\rangle$, i.e.,

$$R = \frac{1}{t}\iiint\left[\sum_{j,j',j''} P_{if}\, g(\omega_j(\bar{k}_1))\, g(\omega_{j'}(\bar{k}_2))\, g(\omega_{j''}(\bar{k}_3))\, d\omega_j(\bar{k}_1)\, d\omega_{j'}(\bar{k}_2)\, d\omega_{j''}(\bar{k}_3)\right], \tag{30}$$

where R is dependent on a three-phonon process involving the lattice mode frequencies $\omega_j(\bar{k}_1)$, $\omega_{j'}(\bar{k}_2)$, $\omega_{j''}(\bar{k}_3)$ and the sum is taken over the nine allowed values of the j's in Eq. (25).

D. Quantum Statistics

In Eq. (23) we wrote the eigenket $|\psi\rangle$ in terms of phonon occupation numbers $\left\{n\begin{pmatrix}\bar{k}_i\\ j\end{pmatrix}\right\}$. As far as quantum mechanics is concerned these numbers are integers and can be selected arbitrarily, but for a system in thermal equilibrium at temperature T we know that it is harder to populate the higher energy levels according to quantum statistics. Therefore, for the phonon occupation numbers for the initial state $|i\rangle$ we have used the Planck distribution where the $\left\{n\begin{pmatrix}\bar{k}_i\\ j\end{pmatrix}\right\}$'s are chosen according to

$$< n\begin{pmatrix}\bar{k}_i\\ j\end{pmatrix} > = \left(\exp(\hbar\omega_j(\bar{k}_i)/k_B\, T) - 1\right)^{-1}, \tag{31}$$

where $<\ldots>$ denotes the average in thermal equilibrium and k_B is the Boltzmann constant.

III. CALCULATION

A. Transition Rate

To calculate the transition rate R of Eq. (30) we must calculate the matrix elements $|< f|H_{int}|i >|^2$ of H_{int} of Eq. (25) that must be inserted into P_{if} of Eq. (27). Let us first consider the summation over the allowed values of the j's in Eq. (30). For a given $\bar{k}_1,\bar{k}_2,\bar{k}_3$

there are nine non-zero matrix elements describing the transition from the initial state $|i\rangle = \left|n(L);n\binom{\bar{k}_1}{j}, n\binom{\bar{k}_2}{j'}, n\binom{\bar{k}_3}{j''}\right\rangle$ to final states $|f\rangle = \left|n(L) + 1; n\binom{\bar{k}_1}{j} - 1, n\binom{\bar{k}_2}{j'} - 1, n\binom{\bar{k}_3}{j''} - 1\right\rangle$. We have adopted the convention of writing the occupation numbers of only those states that will change during the transition. Thus, $|i\rangle$ is really of the form $|\psi\rangle$ in Eq. (23), where the most probable occupation numbers are given by Eq. (31). The matrix elements for the following cases are:

Case 1. $j = j' = j''$; $|f\rangle = \left|n(L)+1; n\binom{\bar{k}_1}{j} -1, n\binom{\bar{k}_2}{j} -1, n\binom{\bar{k}_3}{j} -1\right\rangle$

$$|\langle f|H_{int}|i\rangle|^2 = \frac{\hbar^4}{4^2}\left(\frac{4\lambda_2}{\sqrt{3}\,(N^3M)^{3/2}}\right)^2 \left(\frac{1}{\mu\,\omega_j(\bar{k}_1)\,\omega_j(\bar{k}_2)\,\omega(\bar{k}_3)\,\Omega}\right)$$

$$(n(L)+1)\, n\binom{\bar{k}_1}{j}\, n\binom{\bar{k}_2}{j}\, n\binom{\bar{k}_3}{j} \quad . \tag{32}$$

There are three terms of the above form for j=1,2,3.

Case 2. $j \neq j' = j''$; $|f\rangle = \left|n(L)+1; n\binom{\bar{k}_1}{j} -1, n\binom{\bar{k}_2}{j'} -1, n\binom{\bar{k}_3}{j'} -1\right\rangle$

$$|\langle f|H_{int}|i\rangle|^2 = \frac{\hbar^4}{4^2}\left(\frac{2\lambda_3}{\sqrt{3}\,(N^3M)^{3/2}}\right)^2 \left(\frac{1}{\mu\,\omega_j(\bar{k}_1)\,\omega_{j'}(\bar{k}_2)\,\omega_{j'}(\bar{k}_3)\,\Omega}\right)$$

$$(n(L)+1)\, n\binom{\bar{k}_1}{j}\, n\binom{\bar{k}_2}{j'}\, n\binom{\bar{k}_3}{j'} \quad . \tag{33}$$

There are six terms of the above form. When we substitute these nine terms into P_{if} appearing in R, Eq. (30), along with the proper $g(\omega_j(\bar{k}))$ of Eq. (29), we find that there are 3 similar integrals for Case 1 and 6 similar integrals for Case 2. Therefore, the form of R in Eq. (30) becomes

$$R = C\,\frac{1}{a}\iiint \frac{n(\alpha x)\ n(\alpha y)\ n(\alpha z)}{xyz}\ g(x)\ g(y)\ g(z)\ \ \delta(\alpha - x - y - z)\ dx\ dy\ dz, \tag{34}$$

where the integral has been made dimensionless by using the following definitions

$$C = \frac{\hbar^2}{\pi}\ \frac{1}{\mu M^3}\ \ \frac{(1/2\ \lambda_2^2 + 1/4\ \lambda_3^2\ )}{(2\pi)^3}\ \left(\frac{27}{\nu_0^5}\right)\ , \tag{35a}$$

$$a = \Omega/\omega_0\ , \tag{35b}$$

$$\alpha = \hbar\omega_0/k_B T = \theta/T\ , \tag{35c}$$

$$\omega(\bar{k}_1) = x\ \omega_0,\ \ \omega(\bar{k}_2) = y\ \omega_0,\ \ \omega(\bar{k}_3) = z\ \omega_0, \tag{35d}$$

$$n(\bar{k}_1) = n(\alpha x) = (\exp(\alpha x) - 1)^{-1},\ n(\bar{k}_2) = n(\alpha y),\ n(\bar{k}_3) = n(\alpha z), \tag{35e}$$

and

$$g(x) = x^2,\ \ g(y) = y^2,\ \ g(z) = z^2\ . \tag{35f}$$

The domain of integration of Eq. (34) must be determined subject to the condition that

$$0 \leqslant x,y,z \leqslant 1, \tag{36}$$

since the lattice frequencies must lie between 0 and ω_o or else $g(\omega_j(\bar{k}))$ in Eq. (29) will be zero.

If we integrate over the variable z, the delta function restricts us to the condition

$$z = a - x - y\ . \tag{37}$$

Eq. (36) gives the following condition

$$0 \leqslant a - x - y \leqslant 1, \tag{38}$$

from which we find that

$$y \geqslant -x + (a - 1),\ \text{(lower limit)} \tag{39}$$

and

$$y \leqslant -x + a.\ \ \text{(upper limit)} \tag{40}$$

Therefore, in the xy plane we must integrate over all values of (x,y) that fall between the upper and lower limits and are common to the unit square in the first quadrant. In our model the ratio of the molecular vibrational frequency to the maximum lattice frequency lies between 2 and 3 for benzene, p-dichlorobenzene, carbon tetrachloride, and cyclohexane, i.e., $2 < a < 3$, whereas for naphthalene the ratio lies between 1 and 2, i.e., $1 < a < 2$.

The domains of integration for these two cases can be seen in Figure 1. However, the formula for R developed by Liebermann[2-4] integrates over the whole unit square without restricting the domain of integration. According to our derivation such an integration would not conserve energy. In the model of Liebermann[2-4]

$$a = \frac{\Omega}{\omega_o} = 3.90,$$

since the lowest molecular vibrational frequency of benzene is $\Omega = 2\pi(1.21 \times 10^{13}s^{-1})$ and the maximum lattice frequency was arbitrarily chosen to be the Debye frequency, $\omega_o=\omega_D \equiv 2\pi(3.1 \times 10^{12}s^{-1})$. In that case the lower limit for the integration domain is the line $y = 2.9-x$, which passes entirely above the unit square. The integration domain is therefore empty and consequently $R = 0$. Liebermann's formula yields a non-zero value of R for $a = 3.90$ and must be in error. There is no way that three phonons, whose maximum possible frequency is ω_o, can give the energy necessary to excite a molecular vibrational mode of frequency $\Omega = 3.90\ \omega_o$.

The explicit form for R of Eq. (34) for the case $2 \leqslant a \leqslant 3$ is

$$R = C \frac{1}{a\alpha^3} \quad I(a,\alpha), \tag{41}$$

where

$$I(a,\alpha) = \int_{x=a-2}^{1} \int_{y=-x+(a-1)}^{1} \frac{\alpha^3\ xy(a-x-y)\ dy\ dx}{(e^{\alpha x} - 1)\ (e^{\alpha y} - 1)\ (e^{\alpha(a-x-y)} - 1)} . \tag{42}$$

We decided that an analytical expression for the function of Eq. (42) would be of more general use than a numerical solution on the computer for a few specific values of a and α. In order to arrive at such an expression, we used the Taylor series expansion.

$$\frac{\alpha x}{e^{\alpha x}-1} = 1 - \frac{\alpha x}{2} + B_1 \frac{(\alpha x)^2}{2!} - B_2 \frac{(\alpha x)^4}{4!} + B_3 \frac{(\alpha x)^6}{6!} - B_4 \frac{(\alpha x)^8}{8!} + \dots , \ |\alpha x| < 2\pi , \tag{43}$$

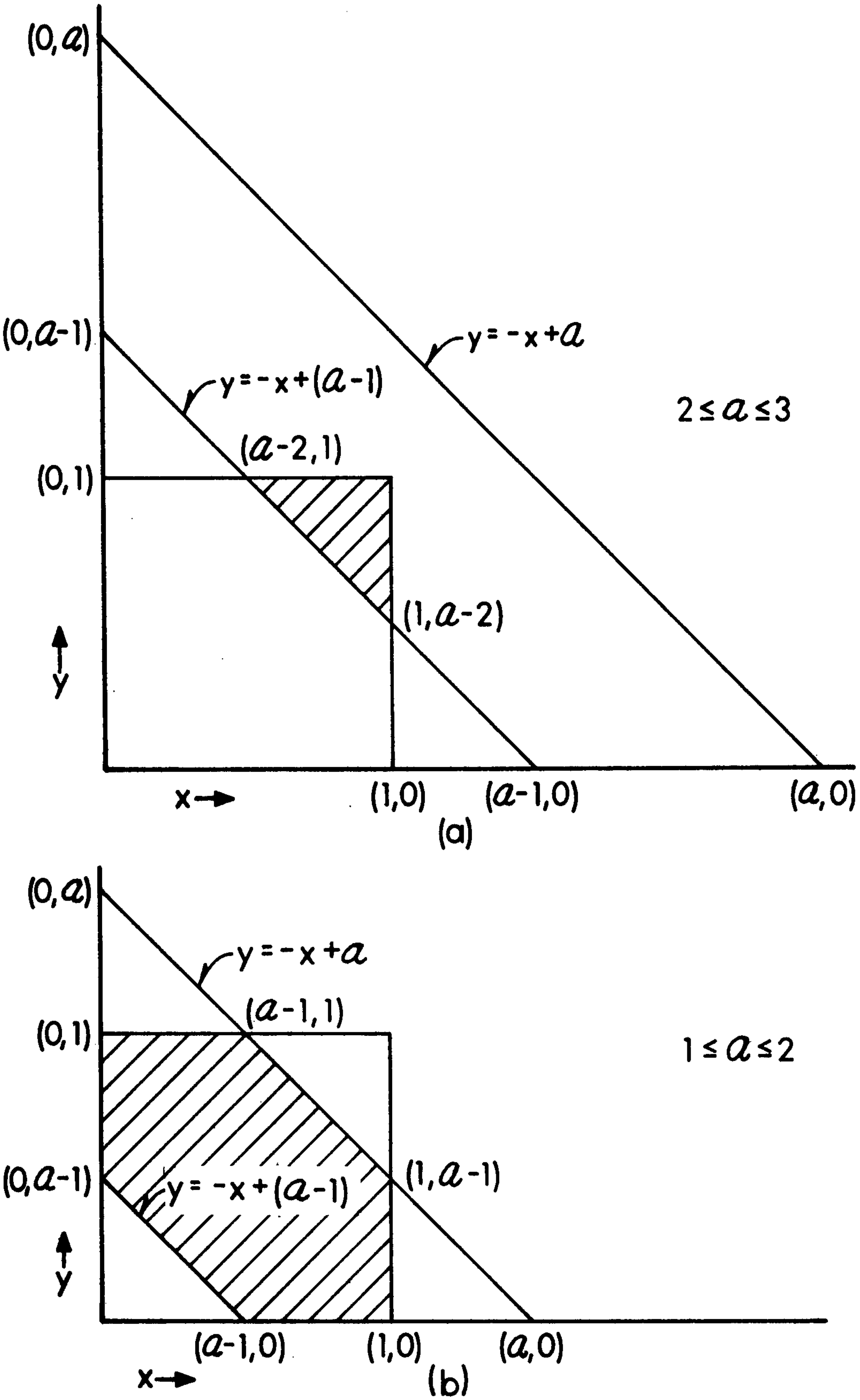

Figure 1. The domain of integration for the transition rate R of Eq. (34) for Case (a), $2 \leqslant a \leqslant 3$, and Case (b), $1 \leqslant a \leqslant 2$.

where the B_n's are the Bernoulli numbers, (B_1 = 1/6, B_2 = 1/30, B_3 = 1/42, B_4 = 1/30, etc.). When we substituted Eq. (43) and the similar expressions for αy and $\alpha(a-x-y)$ into Eq. (42), we obtained a power series in α of the form

$$I(a,\alpha) = (3-a)^2 \sum_{n=0}^{\infty} c_n(a)\, \alpha^n \,, \tag{44}$$

where we evaluated c_n for n = 0 to n = 9. The first few c_n's were calculated by hand, but as this task became exceedingly tedious we relied much more on the values generated by a symbol manipulation program developed by George C. Francis[14] of BRL. In the Appendix A of this BRL Report, we show the integral expressions for the c_n's which will be given here in terms of a only in Table 1.

It is at this part in our paper that we want to point out our disagreement with another approximation which Liebermann made. He truncated the series expansion of Eq. (43) after the first term. But in our calculation for benzene, (as we will show later), α = .965 in Eq. (35) at a temperature of 273K, and the numerical value of $I(a,\alpha)$ of Eq. (44) changes appreciately by retaining higher powers of α.

An alternate expression for $I(a,\alpha)$ in Eq. (42) was pointed out to us by Walter Egerland[15] of BRL. By making three successive substitutions, the variable lower limits of integration are replaced by zero. This form of $I(a,\alpha)$ is better suited to numerical integration on a computer, and also shows how the factor $(3-a)^2$ in Eq. (44) naturally occurs. First, substitute $y \to t-x+a-1$ in the y integration and then substitute $t \to (x-a+2)v$. The resulting integration goes from v=0 to 1. Finally, substitute $x \to (a-2)+(3-a)\,u$ in the x integration. The resulting integration goes from u=0 to 1. Therefore, $I(a,\alpha)$ becomes

$$I(a,\alpha) = \alpha^3 (3-a)^2 \int_{u=0}^{1} \frac{u(p+(1-p)u)}{\left(e^{\alpha[p+(1-p)u]}-1\right)} \tag{45}$$

$$\times \int_{v=0}^{1} \frac{[(1-p)uv-(1-p)u+1]}{\left(e^{\alpha[(1-p)uv-(1-p)u+1]}-1\right)} \frac{[1-(1-p)uv]\,dv\,du}{\left(e^{\alpha[1-(1-p)uv]}-1\right)} \,,$$

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[14] George C. Francis, "SYMAP2 - An Operational Computer Based Algebraic Symbol Manipulator", BRL Memorandum Report No. 2199, (AD 746 957), June 1972.

[15] Walter Egerland, private communication.

TABLE 1. VALUES OF THE C_n's ARE LISTED AS A FUNCTION OF $a = \Omega/\omega_0$.

C_0	$1/2$
C_1	$-a/4$
C_2	$(5a^2+2a-3)/96$
C_3	$-(a^3+2a^2-3a)/192$
C_4	$(13a^4+162a^3-165a^2-228a+162)/86{,}400$
C_5	$(a^5-6a^4-30a^3+114a^2-81a)/86{,}400$
C_6	$(67a^6-2910a^5+13{,}941a^4-21{,}120a^3-9{,}324a^2+40{,}140a-17{,}838)/152{,}409{,}600$
C_7	$(-23a^7+132a^6+747a^5-6{,}198a^4+16{,}569a^3-20{,}070a^2+8{,}919a)/152{,}409{,}600$
C_8	$(-364a^8+8706a^7-60{,}318a^6+184{,}218a^5-234{,}270a^4-58{,}608a^3+533{,}637a^2-562{,}266a+176{,}931)$ $/2.286144 \times 10^{10}$
C_9	$(11a^9-74a^8-448a^7+6058a^6-26{,}610a^5+62{,}262a^4-84{,}068a^3+62{,}474a^2-19{,}659a)$ $/5.08032 \times 10^9$

where

$$p = a - 2, \quad u = (x-p)/(1-p), \quad \text{and} \quad v = (y+x-p-1)/(x-p). \tag{46}$$

An expansion of $I(a,\alpha)$ in power series of $a-3$ is shown in Appendix B. For values of $\alpha < 1$ we obtained numerical agreement with Eq. (44) by using the first four non vanishing terms of that expansion. However, we prefer Eq. (44) where the temperature dependence is in the form of a power series in T^{-1} rather than complicated exponential factors for the latter case.

B. Application to Real Crystals

Up to this part of our paper we have described how to calculate the transition rate for a hypothetical molecular crystal with simple cubic structure and central and noncentral forces. Now we will discuss the approximations we used to treat actual molecular crystals. Liebermann[2-4] assumed that the crystal structure of benzene, which is simple orthorhombic, could be approximated by a simple cubic structure with the length of the cube, d, assumed to be the nearest neighbor distance. We have made the same assumption for benzene, as well as for cyclohexane[5] and carbon tetrachloride[8], which are face-centered cubic, and p-dichlorobenzene[6] and naphthalene[6,7], which are monoclinic C. We have used the data contained in the above papers and listed in Table 2 to calculate the central force constant γ_c, i.e.,

$$\gamma_c = 2\lambda_1 \tag{47}$$

where λ_1 is defined in Eq. (3a). The results are given in Table 3.

For the noncentral force constant we were faced with the following dilemma. We had no information on what noncentral forces to use, and yet if we used only central forces and a simple cubic lattice, we would have three independent linear chains in the x,y, and z directions. Our model would reduce to a one dimensional problem with the density of states $g(\omega_j(k))$ the same as for the linear chain. Therefore, we decided to determine the noncentral force constant γ_{nc} arbitrarily by making it consistent with the known Debye frequency ν_D as reported in the aforementioned papers. Using Eq. (28) with the relation $\omega_D = 2\pi\nu_D$ and Eq. (15) with the relation $\omega_o = 2\pi\nu_o$, we determined γ_{nc} and the maximum lattice frequency to be used in Eq. (29). The results are listed in Table 3. To determine λ_1, λ_2, and λ_3 of Eq. (3), we used the information in Table 2 and listed the results in Table 4. Finally, using values of $k_B = 1.3806 \times 10^{-16}$ erg-K^{-1} and $\hbar = 1.0542 \times 10^{-27}$ erg-s, we calculated values of the constant C in Eq. (35a) for the various substances and also evaluated the constant a in Eq. (35b)

Table 2. Constants Compiled From Other Investigator's Papers.

	$\eta(10^{-14}erg)$	$\sigma(10^{-8}cm)$	$d(10^{-8}cm)$	$M(10^{-22}g)$	$\mu(10^{-23}g)$	$\nu_D(10^{12}s^{-1})$	$\nu_{01}(10^{12}s^{-1})$
benzene[2-4]	6.07	5.27	5.03	1.297	3.987	3.1	12.1
naphthalene[6]	31	3.375	3.75	2.142	3.821	2.7	5.28
p-dichlorobenzene[6]	23	3.6	4.00	2.441	1.678	3	6.8
carbon tetrachloride[8]	4.51	5.88	5.89	2.555	5.930	2	6.51
cyclohexane[5]	4.47	6.093	6.3	1.398	2.326	2.0747	6.24

Table 3. Central and Noncentral Force Constants, and Maximum Lattice Frequency.

	$\gamma_c(10^4g/s^2)$	γ_{nc}/γ_c	$\nu_o(10^{12}s^{-1})$
benzene	3.671	.02619	5.493
napthalene	3.674	.03669	4.319
p-dichlorobenzene	2.454	.03748	3.306
carbon tetrachloride	1.033	.1303	2.272
cyclohexane	.5753	.1416	2.313

Table 4. Evaluation of Constants λ_1, λ_2, and λ_3.

	$\lambda_1(10^4 g/s^2)$	$\lambda_2(10^{20} g/cm^2 s^2)$	$\lambda_3(10^{20} g/cm^2 s^2)$
benzene	1.836	1.729	-1.412
napthalene	1.837	4.064	-2.955
p-dichlorobenzene	1.227	2.329	-1.693
carbon tetrachloride	.5165	.3723	- .2972
cyclohexane	.2877	.1883	- .1473

Table 5. Evaluation of Constants C, Θ, and *a*.

	$C(10^9\ s^{-1})$	$\Theta = \hbar\omega_o/k_B$ (K)	a
benzene	1.764	263.5	2.203
napthalene	7.124	207.2	1.223
p-dichlorobenzene	13.699	158.6	2.057
carbon tetrachloride	.5878	109.0	2.865
cyclohexane	2.118	111.0	2.698

and the ratio $\frac{\hbar\omega_o}{k_B} = \Theta$ in Table 5.

We now have enough information to check our results for benzene[2-4], p-dichlorobenzene[6], carbon tetrachloride[8], and cyclohexane[5] against those of previous investigators, who measured the absorption at the temperatures indicated in Table 6, and determined R_{expt} from a gas phase expression used by Liebermann. The expression for the absorption of ultrasound given by Liebermann[2-4] is

$$\beta = \frac{1}{2V} \frac{(C_p - C_v)}{C_p} \frac{C'}{(C_p - C')} \frac{\omega^2 R_{expt}}{(\omega^2 + R_{expt}^2)} , \tag{48}$$

where β is the absorption, V the velocity of sound, C_p, C_v are the specific heats at constant pressure and constant volume, C' is the specific heat associated with that part of the molecular energy which relaxes, ω is the circular frequency of the sound wave, and R_{expt} is the transition rate. Liebermann[2-4] implies that his expression Eq. (48), has some connection with a similar expression for the absorption of ultrasound in a molecular gas found in a paper by Richards[16]. After changing the notation in Richards' paper, his expression becomes,

$$\beta = \frac{1}{2V} \frac{(C_p - C_v)\ C'\ \omega^2 f_{10}}{C_p C_v f_{10}^2 + (C_p - C')\ (C_v - C')\ \omega^2} \tag{49}$$

where f_{10} is the transition rate for the molecule to go from 1 → 0 and is related to our transition rate R in Eq. (41) by

$$f_{10} \equiv \exp\ (\hbar\ \Omega/k_B\ T)\ R \quad , \tag{50}$$

while

$$f_{01} \equiv R \ , \tag{51}$$

where f_{01} is the transition rate for the molecule to go from 0 → 1. The expression of Richards, Eq. (49), was first developed for a two-state system where the relaxation time τ is related to the transition rates in the usual way, viz.,

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[16] W.T. Richards, "Supersonic Phenomena", Revs. Modern Phys. 11, 36 (1939).

Table 6. Data used to calculate the experimental transition rate f_{10} from Eq. (48) or Eq. (49), usually under the assumption that $f_{10} \gg \omega$.

	Temperature (K)	$\beta(\mathrm{cm}^{-1})$	$\nu=\omega/2\pi(\mathrm{cps})$	V(cm/s)	$C_p(\frac{\mathrm{cal}}{\mathrm{mole\text{-}deg}})$	C_v	C'
benzene[2-4,18]	273	.09	6.4×10^6	3.1×10^5	30.25	21.84	1.38
p-dichlorobenzene[6]	294	.032	5×10^6	2.08×10^5	32	22	1.78
carbon tetrachloride[8]	243	$\beta/\nu^2=2.6 \times 10^{-15}$		1.6×10^5	29	24.7	1.74
cyclohexane[5]	260	.10	4.54×10^6	1.85×10^5	31	26	5.4

$$\frac{1}{\tau} = f_{10} + f_{01} \quad . \tag{52}$$

However, Richards[16] then noted that f_{01} must be neglected when terms involving $\exp(-2h\nu_{01}/k_BT)$ are dropped, i.e.,

$$\frac{1}{\tau} = f_{10} \quad . \tag{53}$$

Richards' expression also agrees with an expression for β found in Eq. (16-15) and Eq. (11-19) in the book by Herzfeld and Litovitz[17], provided that τ is set equal to $1/f_{10}$. Although other approximations for the relaxation time can be used in Eq. (49) we have assumed upon reading Liebermann's papers that R_{expt} in Eq. (48) is

$$R_{expt} \equiv f_{10} \quad , \tag{54}$$

because of the similarity between Eq. (48) and Eq. (49). We prefer Richards' Eq. (49) over Liebermann's Eq. (48) because a derivation is given of the former[16,17] whereas the latter is stated with no derivation[2-4]. In Table 6 all the information necessary to calculate an experimental value of f_{10} from either Eq. (48) or Eq. (49) is given. With the exception of the specific heats for benzene, which were graphically extrapolated from a paper by Lord, Ahlberg, and Andrews[18], all the data in Table 6 are taken from the papers of the previous investigators. Finally, we have used our Eq. (41) to calculate $f_{01} \equiv R$, and thereby f_{10} and have compared it to the experimental value of f_{10} from Liebermann's Eq. (48) and Richards' Eq. (49) in Table 7.

Our results are in good agreement with experiment, considering the approximations made in our theory as well as in the experiments. Inspection of Table 7 shows better agreement of our theoretical transition rate f_{10} with Richards' experimental f_{10} for benzene and p-dichlorobenzene than with Liebermann's experimental transition rate. For cyclohexane the experimental transition rate of Liebermann and Richards are approximately the same, while Liebermann's value of f_{10} for carbon tetrachloride is more in agreement with our theory than Richards' value. More investigation is needed to determine why Liebermann and Richards have different expressions for the experimental transition rate.

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[17] K.F. Herzfeld, and T.A. Litovitz, "Absorption and Dispersion of Ultrasonic Waves", (Academic Press, NY, 1959), p. 77 and p. 63 respectively.

[18] R.C. Lord, Jr., J.E. Ahlberg, and D.H. Andrews, "Calculation of the Heat Capacity Curves of Crystalline Benzene and Benzene - d_6", J. Chem. Phys. 5, 649 (1937).

Table 7. The theoretical transition rates $R \equiv f_{01}$, and f_{10} as calculated from Eq. (41) and Eq. (50), and compared to the transition rate f_{10} as calculated by using the experimental data in Table 6 in Liebermann's Eq. (48) and Richards' Eq. (49).

		Theoretical Strenzwilk and Yedinak		Experimental Liebermann	Richards
	Temperature (K)	$f_{01} \equiv R(s^{-1})$	$f_{10}(s^{-1})$	f_{10}	f_{10}
benzene	273	9.16×10^{7}	7.68×10^{8}	3.86×10^{8}	5.09×10^{8}
p-dichlorobenzene	294	1.06×10^{10}	3.22×10^{10}	1.36×10^{9} [a]	1.88×10^{9}
carbon tetrachloride[b]	243	2.12×10^{7}	7.66×10^{7}	4.49×10^{8}	4.96×10^{8}
cyclohexane	260	2.55×10^{8}	8.06×10^{8}	7.5×10^{8}	7.37×10^{8}

[a] S.S. Yun, private communication.

[b] The lowest mode, $\nu_{01} = 6.51 \times 10^{12} s^{-1}$, of CCl_4 is doubly degenerate. Therefore, the theoretical f_{10} must be multiplied by the factor 2.

IV. DISCUSSION

We have assumed a coupling between three phonons of lattice energy and the 0 → 1 transition in the lowest vibrational mode of a molecule, situated in a simple cubic lattice described by the MPRN model. Then, with the assumption that the density of states can be approximated by a Debye-like distribution, we calculated the transition rate R for a molecule to absorb energy from the lattice. We made several approximations in order to calculate the transition rate for benzene, p-dichlorobenzene, carbon tetrachloride, and cyclohexane. The most notable are that the actual crystal structures can be approximated by a simple cubic lattice, and that the non-central force constant is determined artificially by making it consistent with the known Debye frequency. We compared our f_{10} against the experimental value f_{10} of the other investigators, which was determined from an expression for absorption in gases by Liebermann[2-4] and Richards[16]. This expression does not account for the differences in absorption actually measured along the a,b,c principal crystal axes by Victor and Beyer[9]. A better expression for absorption must be developed.

When we tried to compare our theoretical transition rate with the theoretical one developed by Liebermann[2-4], we realized that his final expression was incorrect because it failed to conserve energy. Under these circumstances we decided that a comparison of the two expressions was inappropriate, even though the theoretical transition rate developed by Liebermann gives a reasonable value for benzene of $10^9 s^{-1}$.

Our paper suggests several directions for future research. With the expressions that we have developed, a theoretical curve of absorption versus ultrasonic frequency or temperature can be plotted and compared with the corresponding experimental curve. Many experimentalists have suggested that the exact expression for the density of states $g(\omega_i(\bar{k}))$ might be important, instead of the Debye approximation Since the exact density of states is known for the MPRN[10,12] model, the differences in the theoretical transition rate can be compared for this model using our formulas. Finally, the actual crystal structure should be put into the calculation as well as the dependence of the transition rate on molecular arrangements along the different crystal directions.

APPENDIX A

Evaluation of the Integral I(a,α)

The integral I(a,α) is defined in Eq. (42) as

$$I(a,\alpha) = \int_{x=a-2}^{1} \int_{y=-x+(a-1)}^{1} \frac{\alpha^3 xy(a-x-y)\,dy\,dx}{(e^{\alpha x}-1)(e^{\alpha y}-1)(e^{\alpha(a-x-y)}-1)} \,. \qquad \text{(A.1)}$$

The Taylor series expansions of $\alpha x/(e^{\alpha x}-1)$, etc., are given by

$$\frac{\alpha x}{e^{\alpha x}-1} = 1 - \frac{\alpha x}{2} - \sum_{n=1}^{\infty} (-1)^n B_n \frac{(\alpha x)^{2n}}{(2n)!} \,, \qquad \text{(A.2a)}$$

$$\frac{\alpha y}{e^{\alpha y}-1)} = 1 - \frac{\alpha y}{2} - \sum_{n=1}^{\infty} (-1)^n B_n \frac{(\alpha y)^{2n}}{(2n)!} \,, \qquad \text{(A.2b)}$$

and

$$\frac{\alpha(a-x-y)}{e^{\alpha(a-x-y)}-1} = 1 - \frac{\alpha(a-x-y)}{2} - \sum_{n=1}^{\infty} (-1)^n B_n \frac{(\alpha(a-x-y))^{2n}}{(2n)!} \,, \qquad \text{(A.2c)}$$

where the B_n's are the Bernoulli numbers[19], (B_1 = 1/6, B_2 = 1/30, B_3 = 1/42, B_4 = 1/30, etc). When these expansions are substituted into Eq. (A.1), we can generate an approximation to I(a,α) in powers of α. To obtain our final form we have made use of the following relations

$$\int_{d-1}^{1} y^m (d-y)^n \, dy \equiv \int_{d-1}^{1} y^n (d-y)^m \, dy \,, \qquad \text{(A.3)}$$

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[19] M.R. Spiegel, in "Mathematical Handbook of Formulas and Tables" (Schaum's Outline Series, McGraw-Hill, NY, 1968), p. 114.

where $d \equiv a - x$, and

$$\int_{x\,=\,a-2}^{1}\int_{y=d-1}^{1} x^n y^m (d-y)^p dydx \equiv \int_{x=a-2}^{1}\int_{y=d-1}^{1} x^m y^n (d-y)^p dydx \;. \tag{A.4}$$

Rewriting $I(a,\alpha)$, with the help of Eq. (44) we have

$$I(a,\alpha) = \int_{x=a-2}^{1}\int_{y=d-1}^{1}\sum_{n=0}^{\infty}(f_n(x,y)\alpha^n)dydx = (3-a)^2\sum_{n=0}^{\infty}c_n\alpha^n, \tag{A.5}$$

where the integrand $f_n(x,y)$ obeys the following relation

$$(3-a)^2 c_n = \int_{x=a-2}^{1}\int_{y=d-1}^{1} f_n(x,y)dydx \;. \tag{A.6}$$

We list the f_n's in Table I. The c_n's have already been given as a function of a in Table 1.

Table I. The integrand $f_\eta(x,y)$ corresponding to the constant c_n for the cases $n = 0$ to $n = 9$.

n	$f_n(x,y)$	c_n
0	1	c_o
1	$-3x/2$	c_1
2	$3xy/4 + 3B_1x^2/2$	c_2
3	$-xy(d-y)/8 - 3B_1x^2y/2$	c_3
4	$3B_1^2x^2y^2/4 - 3B_2x^4/4! + 3B_1x^2y(d-y)/8$	c_4
5	$3B_2x^4y/4! - 3B_1^2xy^2(d-y)^2/8$	c_5
6	$3B_3x^6/6! - 3B_1B_2x^2y^4/4! - 3B_2x^4y(d-y)/4\cdot 4! + B_1^3x^2y^2(d-y)^2/8$	c_6
7	$-3B_3x^6y/6! + 3B_1B_2x^4y^2(d-y)/2!4!$	c_7
8	$3B_1B_3x^2y^6/6! + 3B_2^2x^4y^4/4!4! + 3B_3xy^6(d-y)/4\cdot 6! - 3B_1^2B_2x^2y^4(d-y)^2/4\cdot 4! - 3B_4y^8/8!$	c_8
9	$-3B_1B_3xy^6(d-y)^2/2\cdot 6! - \dfrac{3B_2^2xy^4(d-y)^4}{2\cdot 4!4!} + \dfrac{3B_4x^8y}{8!}$	c_9

APPENDIX B

Taylor Series Expansion of $I(a,\alpha)$ About the point $a = 3$.

The integral $I(a,\alpha)$ is defined in Eq. (45) as

$$I(a,\alpha) = \alpha^3(3-a)^2 \int_{u=0}^{1} \frac{u(p+(1-p)u)}{(e^{\alpha(p+(1-p)u)}-1)} \int_{v=0}^{1} \frac{((1-p)uv-(1-p)u+1)}{(e^{\alpha((1-p)uv-(1-p)u+1)}-1)} \cdot \frac{(1-(1-p)uv)}{(e^{\alpha(1-(1-p)uv)}-1)} \, dvdu \quad , \tag{B.1}$$

where

$$p = a - 2, \tag{B.2}$$

and

$$0 \leqslant p \leqslant 1, \text{ i.e., } 2 \leqslant a \leqslant 3 \ . \tag{B.3}$$

The Taylor series expansion of $I(a,\alpha)$ about the point $a = 3$, is

$$I(a,\alpha) = \alpha^3(a-3)^2 \Bigg[\frac{1}{2(e^\alpha-1)^3} + \frac{((1-\alpha)e^\alpha-1)}{2(e^\alpha-1)^4}(a-3) + \frac{[e^{2\alpha}(2\alpha^2-4\alpha+1)+e^\alpha(\alpha^2+4\alpha-2)+1]}{8(e^\alpha-1)^5}(a-3)^2 + \frac{[e^{3\alpha}(1-15\alpha+30\alpha^2-10\alpha^3)+e^{2\alpha}(-3-30\alpha-15\alpha^2-18\alpha^3)+e^\alpha(3-15\alpha-15\alpha^2-3\alpha^3)-1](a-3)^3}{120(e^\alpha-1)^6} + \cdots \Bigg] , \tag{B.4}$$

where we have considered α to be fixed.

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