

## Theory of Infrared Absorption by Crystals in the High-Frequency Wing of Their Fundamental Lattice Absorption\*

D. L. Mills and A. A. Maradudin

*Department of Physics, University of California, Irvine, California 92664*

*and Xonics Corporation, Van Nuys, California 91406*

(Received 5 February 1973)

We have calculated the frequency dependence of infrared absorption in the classical limit for an exactly soluble model of a lattice of noninteracting diatomic molecules, each bound internally by a potential for which the classical equation of motion can be solved in closed form. Four potentials have been used: a Morse potential, a potential of the form  $V(x) = a/x^2 + bx^2$ , an infinite-square-well potential, and a triangular-well potential. The analytic results we obtain show that the absorption coefficient for large frequencies associated with potentials which admit an harmonic approximation decreases nearly exponentially over the frequency region covered by recent experiments, with significant deviations from exponential behavior at higher frequencies. For the square- and triangular-well potentials, the absorption decreases as  $\omega^{-2}$  for frequencies large compared to a characteristic frequency.

### I. INTRODUCTION

The absorption of electromagnetic radiation by the lattice vibrations in anharmonic crystals has received considerable attention from both theorists and experimentalists for many years. However, most studies have focused attention on frequencies either in the near vicinity of the fundamental reststrahl absorption bands, or at frequencies sufficiently low that the dominant portion of the absorption may be accounted for by processes which involve at most two phonons.<sup>1</sup>

Recently, interest has been aroused in the behavior of the absorption coefficient at frequencies several times (say, 2–10 times) the maximum vibrational frequency of the crystal, but still small compared to the electronic band gap. In this frequency region, the principal contribution to the absorption coefficient in a pure crystal presumably comes from multiphonon processes, where the number of phonons involved may be quite large. The behavior of the absorption coefficient in this frequency regime is clearly important to understand for fundamental physical reasons. There is also a great deal of practical interest in this region, since high-power CO<sub>2</sub> lasers produce intense beams of radiation at 10.6  $\mu$ . This corresponds to a frequency several times that of the maximum vibrational frequency of many materials that may prove useful for the fabrication of windows and lenses for use with these devices. Because the radiation from these lasers is very intense, even a small amount of absorption can lead to appreciable heating of any window through which the beam passes. It is therefore of interest to understand the nature of the intrinsic absorption processes, as well as impurity- and surface-induced absorption at frequencies high compared to the character-

istic vibrational frequencies of the crystal.

One may readily come to appreciate the difficulty of carrying out a first-principles calculation of the frequency dependence of the absorption coefficient in the multiphonon regime for a realistic model of an anharmonic crystal lattice. What is quite intriguing is that experimental studies of the frequency dependence of the absorption coefficient in several alkali halide crystals<sup>2</sup> have revealed that in all the cases studied, for frequencies in the region 200–800 cm<sup>-1</sup>, the absorption coefficient at room temperature may be fitted quite accurately by the empirical formula

$$\beta(\omega) = A e^{-B\omega}, \quad (1.1)$$

where  $\beta(\omega)$  is the absorption coefficient at frequency  $\omega$ , and  $A$  and  $B$  are constants characteristic of the particular crystal. It is extremely important to know whether Eq. (1) can be derived from a theoretical model of some generality and, if so, it is important to know if it holds to frequencies as high as 10.6  $\mu$  and also if it holds at temperatures higher than room temperature.

In this paper, we wish to address ourselves to these questions. Because of the difficulty of carrying out calculations of the absorption coefficient in the multiphonon regime that are both realistic and that lead to conclusions of a general nature, we have chosen to explore the properties of a model of a solid that is highly schematic, but which allows simple analytic expressions to be obtained for the absorption coefficient for a variety of interatomic potentials. We replace a diatomic solid which consists of  $N$  unit cells by an array of  $N$  electric-dipole-active, but anharmonic, oscillators. While such a model is rather oversimplified if we choose to represent a real solid by it, by an examination of the model we can gain insight into

the question of whether the form in Eq. (1.1) is valid quite generally. If it is valid quite generally, it should also be valid for our model. If a realistic potential is chosen for the anharmonic oscillator, we think the model also provides a reliable semiquantitative estimate for the magnitude of the absorption in the multiphonon regime. On the basis of our model, we will also be led to the conjecture that at high frequencies the magnitude of the absorption coefficient might be quite sensitive to the presence of certain impurities.

Since the region of experimental interest to date is room temperature and above, we have used the methods of classical physics to compute the absorption coefficient. We obtain a general expression for the absorption coefficient for the model described above, and then apply the expression to the study of the frequency dependence of the absorption coefficient for four potential functions. We consider absorption by anharmonic oscillators described by the Morse potential, a second potential which possesses a hard core and admits an harmonic approximation [ $V(x) = bx^2 + a/x^2$ ], the square well, and a potential of triangular shape.

The outline of the paper is as follows: In Sec. II, we obtain a general expression for the absorption coefficient of the oscillator array by the use of the methods of classical statistical mechanics. In Sec. III, we apply this expression to the four examples mentioned in the preceding paragraph. In Sec. IV, we present a discussion of some implications of the results obtained in Sec. III.

Quite recently, McGill, Hellwarth, Mangir, and Winston<sup>3</sup> have also presented a theoretical discussion of multiphonon absorption by an array of uncoupled oscillators. In the body of this paper, these authors present a diagrammatic calculation of the absorption coefficient which they argue leads to an exponential form identical to that displayed in our Eq. (1.1) for a specific model of the interatomic potential. Their model presumes that in the crystal Hamiltonian the term proportional to the  $n$ th power of the atomic displacements is proportional to only the quantity  $g^{n-2}/n!$ , where  $g$  is independent of  $n$ , and the factor  $n!$  apparently comes from the Taylor-series expansion of the crystal potential. This model is quite specific, since one may find a large variety of realistic potentials that admit an harmonic approximation and for which their factor  $g^n$  will be replaced by a quantity that exhibits a fundamentally different dependence on  $n$ . (Consider the Lennard-Jones 6-12 potential, or any potential that contains a term which varies inversely with a power of the interatomic separation.) Their conclusion that the absorption coefficient varies exponentially with frequency follows upon counting the number of important diagrams in the first few orders of perturbation

theory. In view of the discussion in the following paragraph and Sec. IV of the present paper, we are led to question the conclusion that for a potential of general form, the theory produces an analytic expression for the absorption coefficient exponential in character in the multiphonon regime.

In Appendix A of their paper, McGill *et al.*<sup>3</sup> consider an array of noninteracting oscillators, each of which is described by a Morse potential. They insert the expression exhibited by Heaps and Herzberg<sup>4</sup> for the appropriate electric dipole moment matrix element into the quantum-mechanical form for the absorption coefficient. A simple analytic expression for the absorption coefficient of the model follows from this procedure. If  $\omega_0$  is the maximum vibration frequency of the crystal, then when  $k_B T > \hbar\omega_0$  the correspondence principle applies, and their expression may be compared with the result we obtain below. The two results agree in this regime. However, while both results provide a rather good fit to the room-temperature data in the regime of frequencies explored by Deutsch, and thus appear qualitatively consistent with the form in Eq. (1.1), at higher frequencies significant deviations are predicted by both expressions. As the temperature is increased, these deviations are expected to set in at progressively lower frequencies. Neither our calculation nor that presented in the appendix of the paper of McGill *et al.* produces an analytic expression for the absorption coefficient of an array of independent oscillators which exhibits the exponential behavior suggested by Eq. (1.1), although, as remarked above, the quantitative differences are small in the frequency regime explored by the experiments so far. Thus, while one may construct a particular potential that leads to something close in form to an exponential law, we feel that quite generally the exponential law is not valid and one may fit the data quite well by the forms we obtain below.

In contrast with the nonperturbative approach to the problem of multiphonon absorption taken in this paper, in a recent paper Sparks and Sham<sup>4a</sup> have calculated multiphonon contributions to the absorption coefficient of crystals of the rocksalt and zincblende structures by many-body perturbation theory. Their analysis yields an absorption coefficient which is consistent with the experimental data.<sup>2</sup>

## II. GENERAL THEORY

Since we consider the crystal to be an array of noninteracting molecules, infrared absorption by the collection of oscillators will be  $N$  times that of a single molecule, where  $N$  is the number of molecules in the crystal. Thus, in what follows, we consider only the absorption by a single molecule. For this the motion of the center of mass of

the molecule is irrelevant, since it makes no contribution to its dipole moment. Consequently, the equation of motion which provides the starting point for our treatment is

$$m\ddot{x} = \dot{p} = -\frac{dV(x)}{dx} + \frac{dM(x)}{dx}E(t), \quad (2.1)$$

where  $m$  is the reduced mass of the molecule,  $x$  is the relative coordinate of the two atoms comprising the molecule with  $p$  the momentum canonically conjugate to  $x$ ,  $V(x)$  is the interaction potential energy between these two atoms,  $M(x)$  is the dipole moment of the molecule, and  $E(t)$  is the electric field of the incident infrared radiation.

To obtain the rate at which energy is absorbed by the molecule from the electromagnetic field, we multiply both sides of Eq. (2.1) by  $\dot{x}$  and rewrite the result in the form

$$\frac{d}{dt} \left[ \frac{1}{2} m \dot{x}^2 + V(x) \right] = E(t) \frac{dM(x)}{dx}. \quad (2.2)$$

The left-hand side of this equation is the instantaneous time rate of change of the energy of the molecule; we denote it by  $d\mathcal{E}/dt$ . It is not the instantaneous time rate of change of the energy in the molecule we require, but rather its average with respect to the canonical ensemble described by the Hamiltonian for the system,

$$\begin{aligned} H &= p^2/2m + V(x) - M(x)E(t) \\ &= H_0 - M(x)E(t), \end{aligned} \quad (2.3)$$

and the time average of the resulting expression.

The average with respect to the canonical ensemble can be expressed in the form

$$\begin{aligned} \left\langle \frac{d\mathcal{E}}{dt} \right\rangle &= \int_{-\infty}^{+\infty} dp \int_{-\infty}^{+\infty} dx \rho(x, p, t) \frac{d\mathcal{E}}{dt} \\ &= \int_{-\infty}^{+\infty} dp \int_{-\infty}^{+\infty} dx \rho(x, p, t) E(t) \frac{dM(x)}{dx}, \end{aligned} \quad (2.4)$$

where  $\rho(x, p, t)$  is the canonical distribution function which obeys the Liouville equation

$$\frac{\partial \rho}{\partial t} + \frac{\partial \rho}{\partial x} \frac{\partial H}{\partial p} - \frac{\partial \rho}{\partial p} \frac{\partial H}{\partial x} = 0. \quad (2.5)$$

In view of Eq. (2.3), this equation can be rewritten as

$$\frac{\partial \rho}{\partial t} + \frac{\partial \rho}{\partial x} \frac{\partial H_0}{\partial p} - \frac{\partial \rho}{\partial p} \frac{\partial H_0}{\partial x} = -\frac{\partial \rho}{\partial p} \frac{dM(x)}{dx} E(t). \quad (2.6)$$

We now expand  $\rho$  in powers of the driving electric field of the infrared radiation,

$$\rho = \rho_0 + \rho_1 + \dots, \quad (2.7)$$

where the subscript denotes the order of the corresponding term in  $E(t)$ . When we substitute the expansion of Eq. (2.7) into Eq. (2.6), and equate

terms of like order in  $E(t)$  on both sides of the equation, we obtain the system of equations

$$\frac{\partial \rho_0}{\partial t} + \frac{\partial \rho_0}{\partial x} \frac{\partial H_0}{\partial p} - \frac{\partial \rho_0}{\partial p} \frac{\partial H_0}{\partial x} = 0, \quad (2.8)$$

$$\frac{\partial \rho_1}{\partial t} + \frac{\partial \rho_1}{\partial x} \frac{\partial H_0}{\partial p} - \frac{\partial \rho_1}{\partial p} \frac{\partial H_0}{\partial x} = -\frac{\partial \rho_0}{\partial p} \frac{dM}{dx} E(t), \quad (2.9)$$

...

We now use the results that

$$\frac{\partial H_0}{\partial p} = \frac{p}{m} = \dot{x}, \quad (2.10a)$$

$$\frac{\partial H_0}{\partial x} = \frac{dV}{dx} = -\dot{p}. \quad (2.10b)$$

Equations (2.8) and (2.9) can then be rewritten as

$$\frac{d}{dt} \rho_0 = 0, \quad (2.11)$$

$$\frac{d}{dt} \rho_1 = -\frac{\partial \rho_0}{\partial p} \frac{dM}{dx} E(t), \quad (2.12)$$

where  $d\rho_0/dt$  and  $d\rho_1/dt$  are the total time derivatives of  $\rho_0$  and  $\rho_1$ , respectively. From a physical point of view,  $d\rho/dt$  is the change in the distribution function seen by an observer moving with a particle that traverses the orbit generated by the Hamiltonian  $H_0$  and which passes through the point  $(x, p)$  in phase space at time  $t$ .

For the equilibrium distribution function  $\rho_0$  we assume the canonical form

$$\rho_0 = e^{-\beta H_0}/Z, \quad \beta = 1/k_B T \quad (2.13)$$

where the partition function  $Z$  is defined by

$$Z = \int_{-\infty}^{+\infty} dp \int_{-\infty}^{+\infty} dx e^{-\beta H_0}. \quad (2.14)$$

If we now use the fact that

$$\frac{\partial \rho_0}{\partial p} = \frac{d\rho_0}{dH_0} \frac{\partial H_0}{\partial p} = -\beta \rho_0 \frac{p}{m} = -\beta \rho_0 \dot{x}, \quad (2.15)$$

Eq. (2.12) for  $\rho_1$  becomes

$$\frac{d\rho_1}{dt} = \beta \rho_0 \dot{x} \frac{dM}{dx} E(t). \quad (2.16)$$

We now assume that the perturbing electric field was switched on adiabatically in the infinitely distant past, so that

$$\rho_1(-\infty) = 0. \quad (2.17)$$

The solution of Eq. (2.16) that obeys the initial condition Eq. (2.17) is

$$\rho_1(t) = \beta \int_{-\infty}^t \rho_0 \dot{x}(t') \left( \frac{dM}{dx} \right)_{x(t'),} E(t') dt'. \quad (2.18)$$

With the results given by Eqs. (2.7), (2.13), and (2.18), we can rewrite Eq. (2.4) in the form

$$\left\langle \frac{d\mathcal{E}}{dt} \right\rangle = \int_{-\infty}^{+\infty} dp \int_{-\infty}^{+\infty} dx \rho_0 \dot{x} \frac{dM(x)}{dx} E(t)$$

$$\begin{aligned}
& + \beta \int_{-\infty}^{+\infty} dp \int_{-\infty}^{+\infty} dx \int_{-\infty}^t \rho_0 \dot{x}(t') \\
& \times \left( \frac{dM}{dx} \right)_{t'} \frac{dM}{dt} E(t') E(t) dt' + \dots \quad (2.19)
\end{aligned}$$

If we use Eqs. (2.3) and (2.13), and rewrite the first term on the right-hand side of Eq. (2.19) in the form

$$E(t) \int_{-\infty}^{+\infty} dp e^{-\beta p^2 / 2m} \frac{p}{m} \int_{-\infty}^{+\infty} dx e^{-\beta V(x)} \frac{dM}{dx}, \quad (2.20)$$

we see that it vanishes because of the vanishing of the integral over  $p$ . Thus, the first nonvanishing contribution to  $\langle d\mathcal{E}/dt \rangle$  comes from the second term. This term may be arranged to read

$$\left\langle \frac{d\mathcal{E}}{dt} \right\rangle = \beta \int_{-\infty}^t \langle \dot{M}(t') \dot{M}(t) \rangle_0 E(t') E(t) dt', \quad (2.21)$$

where we have introduced the notation

$$M(x(t)) = M(t) \quad (2.22)$$

and where for any function  $A(x, p, t)$ ,

$$\langle A \rangle_0 = \int_{-\infty}^{+\infty} dp \int_{-\infty}^{+\infty} dx \rho_0(x, p) A(x, p, t). \quad (2.23)$$

For  $E(t)$ , we now assume the form

$$E(t) = E_0 \cos \omega t e^{\eta t}, \quad (2.24)$$

where  $e^{\eta t}$  is an adiabatic switching factor ( $\eta$  is a positive infinitesimal). With this choice, Eq. (2.21) becomes

$$\begin{aligned}
\left\langle \frac{d\mathcal{E}}{dt} \right\rangle & = \beta E_0^2 \int_{-\infty}^t \langle \dot{M}(t') \dot{M}(t) \rangle_0 \\
& \times \cos \omega t' \cos \omega t e^{\eta(t+t')} dt'. \quad (2.25)
\end{aligned}$$

Let  $t' = t - \tau$ , and integrate over  $\tau$  rather than  $t'$ . Then

$$\begin{aligned}
\left\langle \frac{d\mathcal{E}}{dt} \right\rangle & = \beta E_0^2 e^{2\eta t} \cos \omega t \int_0^\infty \langle \dot{M}(t-\tau) \dot{M}(t) \rangle_0 \\
& \times \cos \omega(t-\tau) e^{-\eta \tau} d\tau. \quad (2.26)
\end{aligned}$$

Because  $H_0$  is time independent, our system possesses time translation invariance, which in the context of the present problem is expressed by

$$\langle \dot{M}(t-\tau) \dot{M}(t) \rangle_0 = \langle \dot{M}(0) \dot{M}(\tau) \rangle_0. \quad (2.27)$$

The time average of Eq. (2.26) thus becomes (in the limit  $\eta \rightarrow 0$ )

$$\left\langle \frac{d\mathcal{E}}{dt} \right\rangle = \frac{1}{2} \beta E_0^2 \int_0^\infty d\tau \cos(\omega \tau) e^{-\eta \tau} \langle \dot{M}(0) \dot{M}(\tau) \rangle_0. \quad (2.28)$$

In Eq. (2.28), we can replace  $\tau$  by  $-\tau$  as an integration variable and use time-reversal symmetry, which leads to the identity

$$\langle \dot{M}(0) \dot{M}(-\tau) \rangle_0 = \langle \dot{M}(0) \dot{M}(\tau) \rangle_0. \quad (2.29)$$

We then obtain an alternative expression for  $\langle \langle d\mathcal{E}/dt \rangle \rangle$ :

$$\left\langle \left\langle \frac{d\mathcal{E}}{dt} \right\rangle \right\rangle = \frac{1}{2} \beta E_0^2 \int_{-\infty}^0 d\tau \cos(\omega \tau) e^{\eta \tau} \langle \dot{M}(0) \dot{M}(\tau) \rangle_0. \quad (2.30)$$

Upon adding half of Eq. (2.28) to Eq. (2.30), we obtain

$$\left\langle \left\langle \frac{d\mathcal{E}}{dt} \right\rangle \right\rangle = \frac{1}{4} \beta E_0^2 \int_{-\infty}^{+\infty} \langle \dot{M}(0) \dot{M}(\tau) \rangle_0 \cos \omega \tau e^{-\eta |\tau|} d\tau \quad (2.31)$$

for the time and thermodynamically averaged rate at which energy is absorbed by a diatomic molecule acted on by an external ac electric field.

The result in Eq. (2.31) may be recognized as a classical version of the well-known Kubo formula for the absorption coefficient.

In what follows, we shall confine our attention to the case of infrared absorption by a first-order dipole moment. That is, if we expand  $M(x)$  in a Maclaurin series,

$$M(x) = M'(0)x + \frac{1}{2} M''(0)x^2 + \dots, \quad (2.32)$$

where the primes denote differentiation with respect to  $x$  (we assume the equilibrium configuration of the molecule has no dipole moment), we retain only the contribution from the leading term in the expansion. McGill *et al.* have examined the effect of the second term on the absorption coefficient and find its effect quantitatively small.<sup>3</sup> The coefficient  $M'(0)$  has the dimensions of a charge, and we denote it by  $q$  in what follows. Thus, the starting point for the investigations in this paper is the following expression for the average rate of energy absorption by a diatomic molecule:

$$\left\langle \left\langle \frac{d\mathcal{E}}{dt} \right\rangle \right\rangle = \frac{\beta q^2 E_0^2}{4m^2} \int_{-\infty}^{+\infty} \langle p(0)p(\tau) \rangle_0 \cos(\omega \tau) e^{-\eta |\tau|} d\tau. \quad (2.33)$$

We next turn to the problem of casting the momentum autocorrelation function  $\langle p(0)p(\tau) \rangle_0$  into a form convenient for computational purposes. This autocorrelation function can be written explicitly in the form

$$\langle p(0)p(t) \rangle_0 = (1/Z) \int_{-\infty}^{+\infty} dp \int_{-\infty}^{+\infty} dx e^{-\beta [p^2 / 2m + V(x)]} p p(t). \quad (2.34)$$

Because the Hamiltonian is time independent, we have expressed it in terms of the values of  $p$  and  $x$  at time  $t=0$  in Eq. (2.34). Thus, here and in what follows  $p$  and  $x$  denote  $p(0)$  and  $x(0)$ , respectively. In addition, as integration of the equations of motion shows, the value of the momentum at time  $t$  is a function of the initial values  $x$  and  $p$ , and we indicate this explicitly by writing  $p(t)$  as  $p(x, p, t)$ .

We now rewrite Eq. (2.34) in the form

$$\begin{aligned}
\langle p(0)p(t) \rangle_0 &= \frac{1}{Z} \int_{-\infty}^{+\infty} dE e^{-\beta E} \int_{-\infty}^{+\infty} dp \int_{-\infty}^{+\infty} dx \\
&\times \delta \left( E - V(x) - \frac{p^2}{2m} \right) p p(x, p, t) \\
&= \frac{m}{Z} \int_{E_{\min}}^{\infty} dE e^{-\beta E} \int_{x_1(E)}^{x_2(E)} dx \int_{-\infty}^{+\infty} dp \\
&\times \frac{\delta(p - p_E) + \delta(p + p_E)}{p_E} p p(x, p, t),
\end{aligned} \tag{2.35}$$

where

$$p_E = \{2m[E - V(x)]\}^{1/2} \tag{2.36}$$

and  $x_1(E)$  and  $x_2(E)$  [chosen so  $x_1(E) \leq x_2(E)$ ] are the classical turning points for motion in the potential  $V(x)$ , i. e., they are the solutions of

$$E = V(x). \tag{2.37}$$

We assume the potential  $V(x)$  is such that there are two classical turning points for energies  $E \geq E_{\min}$ , where  $E_{\min}$  is the minimum value of  $V(x)$ . The physical significance of  $p_E$  is that it is the momentum at  $t=0$  in a motion corresponding to the total energy  $E$ .

Upon carrying out the integration over  $p$  in Eq. (2.35), we obtain

$$\begin{aligned}
\langle p(0)p(t) \rangle_0 &= (m/Z) \int_{E_{\min}}^{\infty} dE e^{-\beta E} \\
&\times \left[ \int_{x_1(E)}^{x_2(E)} dx p(x, p_E, t) \right. \\
&\left. + \int_{x_2(E)}^{x_1(E)} dx p(x, -p_E, t) \right].
\end{aligned} \tag{2.38}$$

Since the momentum at  $t=0$  for  $x$  in the interval  $[x_2(E), x_1(E)]$  is the negative of that at the same point in the interval  $[x_1(E), x_2(E)]$ , because the motion reverses itself at each turning point, the expression in brackets is the integral over one period of the motion beginning at  $x_1(E)$ , and returning to  $x_1(E)$  after one period. Thus, we may write Eq. (2.38) in the form

$$\langle p(0)p(t) \rangle_0 = (m/Z) \int_{E_{\min}}^{\infty} dE e^{-\beta E} \oint dx p(x, p_E, t). \tag{2.39}$$

The one-dimensional motion of a particle in a region bounded by two turning points is a periodic function of time with a period  $T(E)$  given by<sup>5</sup>

$$T(E) = (2m)^{1/2} \int_{x_1(E)}^{x_2(E)} \frac{dx}{[E - V(x)]^{1/2}}. \tag{2.40}$$

This result holds for any initial position  $x$  and momentum  $p_E$  in a motion corresponding to total energy  $E$ . Thus, the integral over a period in Eq. (2.39) is a periodic function of time with the same period  $T(E)$ , and we expand it in a Fourier series:

$$\oint dx p(x, p_E, t) = \sum_{n=-\infty}^{+\infty} p_n(E) e^{-in\omega(E)t}, \tag{2.41}$$

where

$$p_n(E) = \frac{1}{T(E)} \int_0^{T(E)} dt \oint dx p(x, p_E, t) e^{+in\omega(E)t}, \tag{2.42}$$

and we have defined

$$\omega(E) = 2\pi/T(E). \tag{2.43}$$

To obtain a simple expression for  $p_n(E)$ , note that the solution of the equation of motion for a particle moving in a one-dimensional potential is given explicitly by<sup>5</sup>

$$\begin{aligned}
t - t_0 &= \left(\frac{m}{2}\right)^{1/2} \int_{x_1(E)}^x \frac{dx'}{[E - V(x')]^{1/2}}, \\
x_1(E) &\leq x \leq x_2(E).
\end{aligned} \tag{2.44}$$

In writing this expression, we are measuring time with respect to an instant  $t_0$  at which the particle is at the left-hand turning point  $x_1(E)$ . It is necessary to know  $x$  as a function of  $t$  only for  $x_1(E) \leq x \leq x_2(E)$  because as  $t$  increases past  $t_0 + \frac{1}{2}T(E)$ , where  $x = x_2(E)$ , the motion reverses itself [i. e.,  $x(t)$  is symmetric about  $t = t_0 + \frac{1}{2}T(E)$ ] until the time  $t_0 + T(E)$  is reached, at which point the particle has returned to  $x_1(E)$  and the motion begins to repeat again.

The solution of Eq. (2.44) can be written

$$x(t) = x_1(E) + f_E(t - t_0), \tag{2.45}$$

where the function  $f_E(t)$  is an even function of  $t$ , is periodic in  $t$  with period  $T(E)$ , is even about  $t = \frac{1}{2}T(E)$ , and vanishes as  $t \rightarrow 0$ . The momentum  $p_E(t)$  for the orbit of energy  $E$  is

$$p_E(t) = m \frac{df_E(t - t_0)}{dt} = m g_E(t - t_0), \tag{2.46}$$

where  $g_E(t)$  is an odd function of  $t$ , is periodic in  $t$  with period  $T(E)$ , and is odd about  $t = \frac{1}{2}T(E)$ .

With these results, Eq. (2.42) becomes

$$\begin{aligned}
p_n(E) &= \frac{1}{T(E)} \oint dx e^{in\omega(E)t_0} \\
&\times \int_0^{T(E)} dt m g_E(t - t_0) e^{in\omega(E)(t - t_0)},
\end{aligned} \tag{2.47}$$

where the integrations over  $x$  and  $t$  have been interchanged. Since  $g_E(t)$  is periodic with period  $T(E)$ , and we integrate over a complete period, this result becomes

$$\begin{aligned}
p_n(E) &= \frac{i}{T(E)} \oint dx e^{in\omega(E)t_0} \\
&\times \int_0^{T(E)} dt m g_E(t) \sin[n\omega(E)t],
\end{aligned} \tag{2.48}$$

where we have used the fact that  $g_E(t)$  is odd about  $t = \frac{1}{2} T(E)$ . We now convert the first integral from an integral over  $x$  into an integral over  $t_0$ :

$$p_n(E) = \frac{i}{T(E)} \int_0^{-T(E)} dt_0 \frac{dx}{dt_0} e^{i m \omega(E) t_0} \times \int_0^{T(E)} dt m g_E(t) \sin[n\omega(E)t]. \quad (2.49)$$

The coordinate  $x$  is obtained as a function of  $t_0$  by setting  $t = 0$  in Eq. (2.44). The limits on the first integral follow from the fact that the original integral on  $x$  around a period of the motion corresponds to  $t - t_0$  increasing from 0 to  $T(E)$  as  $x$  goes from  $x_1(E)$  to  $x_2(E)$ , and back to  $x_1(E)$ . Setting  $t = 0$ , we see that  $t_0$  goes from 0 to  $-T(E)$  as  $x$  makes the same circuit. Making the change of variable  $t_0 = -t'$ , and using the fact that  $f_E(t)$  in Eq. (2.45) is an even function of  $t$ , we obtain for  $p_n(E)$

$$p_n(E) = \frac{i}{T(E)} \int_0^{T(E)} dt' g_E(t') e^{-i n \omega(E) t'} \times \int_0^{T(E)} dt m g_E(t) \sin[n\omega(E)t] \quad (2.50)$$

or, using the oddness of  $g_E(t')$  about  $t' = \frac{1}{2} T(E)$ , we find finally

$$m p_n(E) = \mathcal{O}_n^2(E) / T(E), \quad (2.51)$$

where

$$\mathcal{O}_n(E) = \int_0^{T(E)} dt p_E(t) \sin[n\omega(E)t], \quad (2.52)$$

where the momentum  $p_E(t) = m g_E(t)$  appearing in Eq. (2.52) must be understood to be obtained from Eq. (2.44) with  $t_0 = 0$  [since that is how  $g(t)$  is defined].

Upon combining Eqs. (2.39), (2.41), (2.43), and (2.51), we obtain for the momentum autocorrelation function

$$\langle p(0)p(t) \rangle_0 = \sum_{n=-\infty}^{+\infty} \int_{E_{\min}}^{\infty} \frac{dE e^{-\beta E}}{2\pi Z} \omega(E) \mathcal{O}_n^2(E) e^{-i n \omega(E) t}. \quad (2.53)$$

$$\begin{aligned} Z &= \int_{-\infty}^{+\infty} dp \int_{-\infty}^{+\infty} dx e^{-\beta [p^2/2m + V(x)]} = \int_{-\infty}^{+\infty} dE e^{-\beta E} \int_{-\infty}^{+\infty} dp \int_{-\infty}^{+\infty} dx \delta(E - V(x) - p^2/2m) \\ &= \int_{E_{\min}}^{\infty} dE e^{-\beta E} \int_{x_1(E)}^{x_2(E)} dx \frac{m}{p_E} \int_{-\infty}^{+\infty} dp [\delta(p - p_E) + \delta(p + p_E)] = \int_{E_{\min}}^{\infty} dE e^{-\beta E} (2m)^{1/2} \int_{x_1(E)}^{x_2(E)} \frac{dx}{[E - V(x)]^{1/2}}, \end{aligned}$$

or finally

$$Z = \int_{E_{\min}}^{\infty} dE e^{-\beta E} T(E). \quad (2.56)$$

We next proceed to apply the results of the present section to the examples mentioned in Sec. I.

When this result is substituted into Eq. (2.33), and the integration over time is carried out, we obtain (as  $\eta \rightarrow 0+$ )

$$\left\langle \left\langle \frac{d\mathcal{E}}{dt} \right\rangle \right\rangle = \frac{\beta q^2 E_0^2}{8m^2 Z} \sum_{n=-\infty}^{+\infty} \int_{E_{\min}}^{\infty} dE e^{-\beta E} \omega(E) \mathcal{O}_n^2(E) \times [\delta(\omega - n\omega(E)) + \delta(\omega + n\omega(E))]. \quad (2.54)$$

If we note that  $\mathcal{O}_n^2(E)$  vanishes for  $n=0$ , and is an even function of  $n$  for  $n \neq 0$ , we finally obtain for the average rate of energy absorption by a diatomic molecule

$$\left\langle \left\langle \frac{d\mathcal{E}}{dt} \right\rangle \right\rangle = \frac{\omega \beta q^2 E_0^2}{4m^2 Z} \sum_{n=1}^{\infty} \frac{1}{n} \int_{E_{\min}}^{\infty} dE \times e^{-\beta E} \mathcal{O}_n^2(E) \delta(\omega - n\omega(E)), \quad (2.55)$$

where we have assumed  $\omega > 0$ .

The dynamics of the problem are seen to enter simply through the necessity of knowing  $p_E(t)$  for the evaluation of  $\mathcal{O}_n(E)$  and  $\omega(E)$ . Moreover, if  $\omega(E)$  is a sufficiently simple function of  $E$  so that the equation  $\omega = n\omega(E)$  can be inverted, the integration over  $E$  can be carried out using properties of the  $\delta$  function.

We briefly summarize in words the procedure for computing the quantities that enter Eq. (2.55). Given a potential function  $V(x)$ , one requires the period  $T(E)$  as a function of energy. This function may be obtained from Eq. (2.40) and  $\omega(E)$  is defined by Eq. (2.43). By solving the equations of motion, one finds the momentum as a function of time  $p_E(t)$  for an orbit of energy  $E$ , with the origin of time chosen so the parameter  $t_0$  in Eq. (2.44) is set equal to zero. The quantity  $\mathcal{O}_n(E)$  is a measure of the amplitude of the  $n$ th harmonic in the function  $p_E(t)$ , and is obtained from Eq. (2.52). Finally,  $Z$  is the partition function.

We conclude the present section by displaying a remarkably simple relation between the partition function of the oscillator, and the function  $T(E)$ , that gives the period as a function of energy.

We have

### III. APPLICATIONS OF THE FORMALISM TO THE STUDY OF MULTIPHONON ABSORPTION FOR SOME SPECIFIC POTENTIALS

In this section, we study the behavior of the absorption coefficient as a function of frequency for four specific forms of the interatomic potential

$V(x)$ . We first derive the form of the absorption coefficient for the Morse potential, a form used frequently in molecular physics. We then consider the potential  $V(x) = ax^2 + b/x^2$ , the square well, and the potential  $V(x) = \gamma x$  for  $x \geq 0$ ,  $V(x) = \infty$  for  $x < 0$ . The last two potentials are interesting examples to consider, since one cannot construct a discussion of a perturbative nature, because an harmonic approximation does not exist for either case.

#### A. Morse Potential

The Morse potential may be written in the form

$$V(x) = D(1 - e^{-a(x-x_0)})^2. \quad (3.1)$$

The minimum value of  $V(x)$  is zero and the minimum occurs at  $x = x_0$ . For large values of the interparticle separation  $V(x)$  approaches the constant value  $D$ , the dissociation energy of the molecule. For most cases of interest here,  $D$  assumes a value of the order of 1 eV, an energy very large compared to  $k_B T$ , as long as we confine our attention to temperatures the order of or lower than the melting temperature of the solids of interest to us. We shall make use of the fact that  $k_B T \ll D$  in the discussion below.

If we consider only motions of small amplitude,  $x$  remains near  $x_0$ , and  $V(x)$  is well approximated by the parabolic form

$$V(x) = D a^2 (x - x_0)^2. \quad (3.2)$$

Thus, in the limit where the amplitude of the motion is small, the molecule behaves like an harmonic oscillator with frequency  $\omega_0$  given by

$$\omega_0^2 = 2a^2 D / m. \quad (3.3)$$

We begin by deriving an expression for the quantity  $p_E(t)$  defined in Sec. II, following the procedure outlined there. We begin with Eq. (2.44), which with  $t_0$  equal zero becomes

$$t = \left(\frac{1}{2} m\right)^{1/2} \int_{x_1(E)}^x dx' \\ \times (E - D + 2De^{a(x_0-x')} - De^{2a(x_0-x')})^{-1/2}. \quad (3.4a)$$

The integral can be evaluated in closed form. This may be done by letting  $\theta = e^{-ax}$  and  $\theta_1 = e^{-ax_1(E)}$ . If we then define  $C = De^{2ax_0}$ ,  $B = 2De^{ax_0}$ , and  $A = D - E$ , the integral becomes

$$t = \frac{1}{a} \left(\frac{m}{2}\right)^{1/2} \int_{\theta_1}^{\theta} (B\theta' - A - C\theta'^2)^{-1/2} \frac{d\theta'}{\theta'}. \quad (3.4b)$$

For bound motions of the molecule, the only case of interest here,  $B\theta \geq A + C\theta^2$  everywhere. The integral is then readily evaluated<sup>6</sup> to give

$$at \left(\frac{2}{m} (D - E)\right)^{1/2} = \sin^{-1} \left( \frac{(D - E) - De^{ax_0\theta'}}{(DE)^{1/2} e^{ax_0\theta'}} \right)_{\theta_1}^{\theta}$$

$$= \sin^{-1} \left( \frac{(D - E) - De^{ax_0\theta}}{(DE)^{1/2} e^{ax_0\theta}} \right) + \frac{\pi}{2}. \quad (3.5)$$

If this relation is solved for  $\theta$  as a function of  $t$ , and  $x(t)$  is obtained from this result, one finds

$$x(t) = x_0 + \frac{1}{a} \ln \frac{D}{D - E} \\ + \frac{1}{a} \ln \left[ 1 - \left(\frac{E}{D}\right)^{1/2} \cos \omega(E)t \right], \quad (3.6)$$

where we have introduced the quantity  $\omega(E)$ , defined by

$$\omega(E) = \omega_0 (1 - E/D)^{1/2}. \quad (3.7)$$

From Eq. (3.6), it is evident that the period  $T(E)$  of the motion is

$$T(E) = 2\pi / \omega(E). \quad (3.8)$$

For small energies,  $T(E)$  assumes a value independent of energy and equal to  $2\pi/\omega_0$ , and the period lengthens as  $E$  increases.

The momentum  $p_E(t)$  is found from  $m\dot{x}(t)$ , with  $x(t)$  given by Eq. (3.6). If this differentiation is carried out and the result substituted into the expression for  $\sigma_n(E)$  given in Eq. (2.52), one obtains

$$\sigma_n(E) = \frac{(2mE)^{1/2} \omega(E)}{\omega_0} \\ \times \int_0^{T(E)} \frac{\sin n\omega(E)t \sin \omega(E)t}{1 - (E/D)^{1/2} \cos \omega(E)t} dt \\ = \frac{2(2mE)^{1/2}}{\omega_0} \int_0^{\pi} \frac{\sin \varphi \sin \varphi}{1 - (E/D)^{1/2} \cos \varphi} d\varphi. \quad (3.9)$$

The integral in Eq. (3.9) may be evaluated exactly, to give<sup>6</sup>

$$\sigma_n(E) = \frac{2\pi(2mE)^{1/2}}{\omega_0} \left(\frac{D}{E}\right)^{(n+1)/2} \left[ 1 - \left(1 - \frac{E}{D}\right)^{1/2} \right]^n. \quad (3.10)$$

The discussion shows that for the Morse potential, exact results for all quantities which enter the expression for the absorption coefficient are readily obtained, for the bound orbits. We shall compute an approximate form for the absorption rate in the limit  $k_B T \ll D$ , where only orbits with energy  $E \ll D$  contribute significantly to the rate of absorption. In this regime, we replace  $\sigma_n(E)$  by its leading contribution when  $E \ll D$ :

$$\sigma_n(E) = \frac{2\pi(2mD)^{1/2}}{\omega_0} \left(\frac{E}{4D}\right)^{n/2}. \quad (3.11)$$

In this limit, the function  $\omega(E)$  may also be replaced by the approximate form  $\omega_0$  independent of energy, for  $E \ll D$ . From Eq. (2.56), one readily sees that the expression for the partition function

becomes

$$Z = 2\pi/\omega_0\beta. \quad (3.12)$$

If these approximations are inserted into the expression for  $\langle\langle d\mathcal{E}/dt \rangle\rangle$  displayed in Eq. (2.55), one finds that

$$\langle\langle \frac{d\mathcal{E}}{dt} \rangle\rangle = \sum_{n=1}^{\infty} \alpha_n \delta(\omega - n\omega_0), \quad (3.13a)$$

where

$$\alpha_n = \frac{\pi}{4} \frac{q^2 E_0^2}{m} n! \left( \frac{k_B T}{4D} \right)^{n-1}. \quad (3.13b)$$

For the case  $n=1$ , we have

$$\alpha_1 = \frac{1}{4} \pi q^2 E_0^2 / m, \quad (3.13c)$$

independent of temperature, the well-known result for the integrated strength of the fundamental absorption line of a simple harmonic oscillator of mass  $m$ , charge  $q$ , and frequency  $\omega_0$ . (Recall that  $E_0$  is the peak value of the field.)

The integrated strength of the absorption peak at the frequency  $\omega = n\omega_0$  (the  $n$ -phonon absorption peak for this model) is related to that of the fundamental absorption peak by the simple relation

$$\frac{\alpha_n}{\alpha_1} = n! \left( \frac{k_B T}{4D} \right)^{n-1}. \quad (3.14)$$

#### B. Potential $V(x) = a/x^2 + bx^2$

The second potential function we consider is

$$V(x) = a/x^2 + bx^2, \quad x \geq 0. \quad (3.15)$$

Setting  $t_0 = 0$  in Eq. (2.44), we obtain for the equation determining  $x(t)$ ,

$$t = \frac{m}{2} \int_{x_1(E)}^x \frac{x dx}{(-a + Ex^2 - bx^4)^{1/2}}. \quad (3.16)$$

The turning points  $x_{1,2}(E)$  are the solutions of the equation

$$E = a/x^2 + bx^2 \quad (3.17)$$

and are found to be

$$x_1(E) = \left( \frac{E - (E^2 - 4ab)^{1/2}}{2b} \right)^{1/2}, \quad (3.18a)$$

$$x_2(E) = \left( \frac{E + (E^2 - 4ab)^{1/2}}{2b} \right)^{1/2}. \quad (3.18b)$$

The energy  $E_{\min}$  equals the minimum value of the potential energy (3.15). Equivalently, it is the energy for which  $x_1(E) = x_2(E)$ , and hence is given by

$$E_{\min} = 2(ab)^{1/2}. \quad (3.19)$$

The change of variable  $x^2 = y$  transforms Eq. (3.16) into

$$t = \frac{1}{2} \left( \frac{m}{2b} \right)^{1/2} \int_{x_1^2(E)}^{x^2} \frac{dy}{(-a + Ey - by^2)^{1/2}} \\ = \frac{1}{2} \left( \frac{m}{2b} \right)^{1/2} \left( \frac{\pi}{2} - \sin^{-1} \frac{E - 2bx^2}{(E^2 - 4ab)^{1/2}} \right). \quad (3.20)$$

If we evaluate this expression for  $x = x_2(E)$ , the left-hand side must be set equal to  $\frac{1}{2} T(E)$ , and in this way we obtain

$$T(E) = \pi(m/2b)^{1/2}. \quad (3.21)$$

Consequently, the frequency  $\omega(E)$  is given by

$$\omega(E) = (8b/m)^{1/2} \equiv \omega_0. \quad (3.22)$$

It should be noted that the period  $T(E)$  and the corresponding frequency  $\omega(E)$  for the potential (3.15) are independent of the energy  $E$ .

It follows immediately from Eqs. (2.56) and (3.21) that the partition function  $Z$  is given by

$$Z = (2\pi/\beta\omega_0) \exp[-2\beta(ab)^{1/2}]. \quad (3.23)$$

Expression (2.55) for the rate at which energy is absorbed by the molecule described by the potential function (3.15) now becomes

$$\langle\langle \frac{d\mathcal{E}}{dt} \rangle\rangle = \frac{\omega\omega_0}{8\pi} \beta^2 \frac{q^2}{m^2} E_0^2 \sum_{n=1}^{\infty} \frac{1}{n} \exp[2\beta(ab)^{1/2}] \\ \times \int_{E_{\min}}^{\infty} dE e^{-\beta E} \rho_n^2(E) \delta(\omega - n\omega_0). \quad (3.24)$$

If we make the change of variable  $E = 2(ab)^{1/2}(z+1)$ , we obtain the convenient form

$$\langle\langle \frac{d\mathcal{E}}{dt} \rangle\rangle = 2(ab)^{1/2} \frac{\omega\omega_0}{8\pi} \beta^2 \frac{q^2}{m^2} E_0^2 \\ \times \sum_{n=1}^{\infty} \frac{1}{n} \left( \int_0^{\infty} dz \exp[-2\beta(abz)^{1/2}] \right. \\ \left. \times \rho_n^2(2(ab)^{1/2}(z+1)) \right) \delta(\omega - n\omega_0). \quad (3.25)$$

Since  $2(ab)^{1/2} = E_{\min}$ , we see that for temperatures such that  $E_{\min} \gtrsim k_B T$ , only values of  $z \lesssim 1$  contribute significantly to the integral. We now turn to a determination of  $\rho_n(E)$ .

Inverting Eq. (3.20) we obtain for  $x(t)$ ,

$$x(t) = \left( \frac{E}{2b} - \frac{(E^2 - 4ab)^{1/2}}{2b} \cos\omega_0 t \right)^{1/2}, \quad (3.26)$$

from which we immediately obtain  $p(t)$ :

$$p(t) = m^{1/2} \frac{(E^2 - 4ab)^{1/2}}{E^{1/2}} \\ \times \frac{\sin\omega_0 t}{\{1 - [(E^2 - 4ab)^{1/2}/E] \cos\omega_0 t\}^{1/2}}. \quad (3.27)$$

The integral  $\rho_n$  in this case is given by

$$\rho_n(E) = 2(mE)^{1/2} \frac{\delta}{\omega_0} \int_0^{\pi} \frac{\sin x \sin nx}{(1 - \delta \cos x)^{1/2}} dx, \quad (3.28)$$



where we have set

$$\delta = (E^2 - 4ab)^{1/2}/E. \quad (3.29)$$

The change of variable  $x = \pi - 2\varphi$  yields the following expression for  $\Phi_n(E)$ :

$$\Phi_n(E) = (-1)^{n-1} \frac{(mE)^{1/2}}{\omega_0} \frac{2\delta}{(1+\delta)^{1/2}} \times \int_0^{\pi/2} \frac{\cos 2(n-1)\varphi - \cos 2(n+1)\varphi}{\{1 - [2\delta/(1+\delta)] \sin^2 \varphi\}^{1/2}} d\varphi. \quad (3.30)$$

The integral

$$K_n(k) = \int_0^{\pi/2} \frac{\cos 2nx}{(1 - k^2 \sin^2 x)^{1/2}} dx, \quad 0 \leq k < 1, \quad n = 0, 1, 2, \dots \quad (3.31)$$

has the following expansion in powers of  $k^2$ :

$$K_n(k) = (-1)^n \frac{\pi}{2} \sum_{\nu=n}^{\infty} \left( \frac{\Gamma(\nu + \frac{1}{2})}{\Gamma(\frac{1}{2})} \right)^2 \times \frac{k^{2\nu}}{(\nu-n)!(\nu+n)!} \quad (3.32a)$$

$$= (-1)^n \frac{\pi}{2} \left( \frac{\Gamma(n + \frac{1}{2})}{\Gamma(\frac{1}{2})} \right)^2 \frac{k^{2n}}{(2n)!} \times \left( 1 + \frac{(2n+1)}{4} k^2 + \frac{(2n+1)(2n+3)}{32(2n+2)} k^4 + \dots \right). \quad (3.32b)$$

Consequently, since in the present case

$$k^2 = 2\delta/(1+\delta) < 1, \quad (3.33)$$

the first two terms in the expansion of  $\Phi_n(E)$  are found to be

$$\Phi_n(E) = \frac{\pi}{2} \frac{(mE)^{1/2}}{\omega_0} \left( \frac{\Gamma(n - \frac{1}{2})}{\Gamma(\frac{1}{2})} \right)^2 \frac{1}{(2n-2)!} \frac{(2\delta)^n}{(1+\delta)^{n-1/2}} \times \left[ 1 + \frac{2n-1}{4} \frac{2\delta}{1+\delta} + O\left( \left( \frac{2\delta}{1+\delta} \right)^2 \right) \right]. \quad (3.34)$$

Consequently, we have that

$$\Phi_n^2(E) \sim \frac{\pi^2}{4} \frac{mE}{\omega_0^2} \left( \frac{\Gamma(n - \frac{1}{2})}{\Gamma(\frac{1}{2})} \right)^4 \frac{1}{[(2n-2)!]^2} \frac{(2\delta)^{2n}}{(1+\delta)^{2n-1}} \times \left[ 1 + \frac{2n-1}{2} \frac{2\delta}{1+\delta} + O\left( \left( \frac{2\delta}{1+\delta} \right)^2 \right) \right]. \quad (3.35)$$

Since  $\delta < 1$ , we can simplify this expression to

$$\Phi_n^2(E) = \pi^2 \frac{mE}{\omega_0^2} \frac{[(2n-2)!]^2}{2^{2n-2} [(n-1)!]^4} \delta^{2n} [1 + O(\delta^2)]. \quad (3.36)$$

If we make the replacement  $E = 2(ab)^{1/2}(z+1)$  in Eq. (3.29), we find that as a function of  $z$ ,  $\delta$  is given by

$$\delta = (z^2 + 2z)^{1/2}/(z+1)$$

$$= (2z)^{1/2} \left[ 1 - \frac{3}{4}z + \frac{23}{32}z^2 + \dots \right], \quad 0 \leq z < 1. \quad (3.37)$$

Thus, the leading term in the expansion of  $\Phi_n^2(2(ab)^{1/2}(z+1))$  for small  $z$  is

$$\Phi_n^2(2(ab)^{1/2}(z+1)) \sim \pi^2 \frac{m}{\omega_0^2} 2(ab)^{1/2} \times \frac{[(2n-2)!]^2}{2^{2n-2} [(n-1)!]^4} z^n + O(z^{n+1}). \quad (3.38)$$

When this result is substituted into Eq. (3.25), and the integral over  $z$  is carried out, we obtain finally

$$\left\langle \left\langle \frac{d\mathcal{E}}{dt} \right\rangle \right\rangle = \frac{\pi}{4} \frac{q^2}{m} E_0^2 \sum_{n=1}^{\infty} \frac{[(2n-2)!]^2 n!}{2^{2n-2} [(n-1)!]^4} \times \left( \frac{k_B T}{E_{\min}} \right)^{n-1} \delta(\omega - n\omega_0). \quad (3.39)$$

We see from this result that the integrated strength of absorption at the frequency  $\omega = \omega_0$ ,  $(\pi q^2/4m)E_0^2$ , is independent of temperature and has the same value as in the case of the Morse potential. The integrated strength of the absorption at the frequency  $\omega = n\omega_0$  is related to that of the fundamental absorption peak ( $n=1$ ) by

$$\frac{[(2n-2)!]^2}{2^{2n-2} [(n-1)!]^4} n! \left( \frac{k_B T}{E_{\min}} \right)^{n-1}, \quad (3.40)$$

which is very close in form to the corresponding relation (3.14) obtained for the Morse potential.

### C. Square Well

We next apply the method to compute the shape of the absorption spectrum for a particle trapped in a square-well potential, with infinitely steep sides. This example is an interesting application of the formalism developed in Sec. II, since the potential does not admit an harmonic approximation. In Sec. IV, we argue that there are certain impurities in alkali halides that may be regarded as moving in a very steep-sided potential that can be approximated by a square well, at least for qualitative purposes.

We suppose that the square well has width  $L$ , with infinitely steep sides. If we consider motion of a particle of mass  $m$  in the well, with energy  $E$ , then the velocity  $v$  of the particle is  $(2E/m)^{1/2}$ . The period  $T(E)$  is  $2L/v$ , or

$$T(E) = L(2M/E)^{1/2} = 2\pi/\omega(E). \quad (3.41)$$

For the momentum  $p_E(t)$ , one has

$$p_E(t) = (2mE)^{1/2}, \quad 0 < t < \frac{1}{2} T(E) \\ = -(2mE)^{1/2}, \quad \frac{1}{2} T(E) < t < T(E). \quad (3.42)$$

A short calculation gives for this potential

$$\Phi_n(E) = (2mL/m)[1 - (-1)^n].$$

It is a straightforward matter to insert this expression into Eq. (2.55), and obtain the form of  $\langle\langle d\mathcal{E}/dt \rangle\rangle$ . The computation of the partition function is also quite elementary. The final result is best expressed in terms of a characteristic frequency  $\omega_T$ , given by

$$\omega_T = \pi(2k_B T/mL^2)^{1/2}. \quad (3.43)$$

In terms of  $\omega_T$ , the expression for the rate of energy absorption is

$$\begin{aligned} \langle\langle \frac{d\mathcal{E}}{dt} \rangle\rangle &= \frac{8}{\pi^{3/2}} \frac{q^2 E_0^2}{m} \frac{\omega^2}{\omega_T^3} \\ &\times \sum_{n=0}^{\infty} \frac{\exp[-\omega^2/\omega_T^2(2n+1)^2]}{(2n+1)^5}. \end{aligned} \quad (3.44)$$

The absorption coefficient is thus a superposition of a sequence of Gaussians. The function on the right-hand side of Eq. (3.44) has a prominent peak very near  $\omega = \omega_T$ , with weak subsidiary maxima at higher frequencies. Of particular interest is the behavior of the absorption coefficient for frequencies large compared to  $\omega_T$ . In this region, one may find the asymptotic form of the absorption coefficient by replacing the sum in Eq. (3.44) by an integration. For  $\omega \gg \omega_T$ , by this means one finds

$$\begin{aligned} \langle\langle \frac{d\mathcal{E}}{dt} \rangle\rangle &\approx \frac{4}{\pi^{3/2}} \frac{q^2 E_0^2}{m} \frac{\omega^2}{\omega_T^3} \int_0^{\infty} \frac{dS}{S^5} \exp\left(-\frac{\omega^2}{\omega_T^2} \frac{1}{S^2}\right) \\ &= \frac{2}{\pi^{3/2}} \frac{q^2 E_0^2}{m} \frac{\omega_T}{\omega^2}. \end{aligned} \quad (3.45)$$

Thus, for frequencies large compared to the characteristic frequency  $\omega_T$ , the square-well potential gives rise to an absorption coefficient that falls off as  $\omega^{-2}$ , a result qualitatively different from the empirical form displayed in Eq. (1.1).

#### D. Triangular Well

We next display the form of the absorption coefficient for a potential  $V(x)$  of the form

$$\begin{aligned} V(x) &= \infty, & x < 0 \\ &= \gamma x, & x > 0 \end{aligned} \quad (3.46)$$

where the constant  $\gamma$  is presumed positive. This is a second example of a potential for which there is no harmonic approximation.

The classical equations of motion for this example are quite elementary. For an orbit with energy  $E$ , the period  $T(E)$  is

$$T(E) = (2/\gamma)(2mE)^{1/2}, \quad (3.47)$$

and the momentum of the particle as a function of time is

$$\begin{aligned} p_E(t) &= (2mE)^{1/2}[1 - 2t/T(E)], & 0 < t < \frac{1}{2}T(E) \\ &= -(2mE)^{1/2}[1 - 2t/T(E)], & \frac{1}{2}T(E) < t < T(E). \end{aligned}$$

A short and straightforward calculation then gives

$$\rho_n(E) = 4mE/\pi\gamma n, \quad (3.48)$$

and for the partition function

$$Z = [(2\pi m)^{1/2}/\gamma](k_B T)^{3/2}. \quad (3.49)$$

When these results are inserted in Eq. (2.55), one finds that the results assume the form

$$\langle\langle \frac{d\mathcal{E}}{dt} \rangle\rangle = \frac{4}{\pi^{5/2}} \frac{q^2 E_0^2}{m} \frac{\Omega_T^5}{\omega^6} \sum_{n=1}^{\infty} n^3 \exp\left(-n^2 \frac{\Omega_T^2}{\omega^2}\right), \quad (3.50)$$

where  $\Omega_T$  is a characteristic frequency given by

$$\Omega_T = \pi\gamma(2mk_B T)^{-1/2}. \quad (3.51)$$

When  $\omega \gg \Omega_T$ , the form of the absorption coefficient may be deduced by replacing the sum over  $n$  by an integration, as we did in the preceding example. In the high-frequency regime, one finds that

$$\langle\langle \frac{d\mathcal{E}}{dt} \rangle\rangle = \frac{2}{\pi^{5/2}} \frac{q^2 E_0^2}{m} \frac{\Omega_T}{\omega^2}, \quad (3.52)$$

a result remarkably similar to that obtained for the square well. In both examples, for  $\omega$  large compared to a characteristic frequency, the absorption falls off as  $\omega^{-2}$ .

#### IV. GENERAL DISCUSSION

The purpose of this section is to examine some implications of the results in Sec. III.

We first examine the question of the validity of the phenomenological form displayed in Eq. (1.1), which is suggested by the absorption data reported to date. If this form is in fact a general result which holds in the limit of high frequencies, then we should expect it to emerge from our analysis. If we consider the Morse potential and also the potential  $bx^2 + a/x^2$ , our independent oscillator model predicts a series of absorption peaks at the frequencies  $\omega_n = n\omega_0$ , where  $\omega_0$  is the fundamental vibration frequency of the anharmonic oscillator. If the exponential law is obeyed for these models, then we should expect the integrated strength of the  $n$ -phonon peak (the absorption peak at  $n\omega_0$ ) to vary with  $n$  as  $\epsilon^n$ , where  $\epsilon$  is a parameter independent of  $n$  that depends on the details of the interatomic potential and the temperature.

If we examine the results obtained in Sec. III, we see that a relation of this form does not hold for any of the four potentials we have examined. The two potentials most directly applicable to real physical systems are the Morse potential and the potential  $bx^2 + a/x^2$ , since both of these potentials admit an harmonic approximation. If we denote the integrated strength of the  $n$ -phonon peak by  $\alpha_n$ , then for the Morse potential we find that

$$\alpha_n = n! (kT/4D)^{n-1} \alpha_1, \quad (4.1)$$

where  $\alpha_1$  is the integrated strength of the fundamental reststrahl band at  $\omega_0$ . A very similar relation obtains for the potential  $bx^2 + a/x^2$ , as we have seen. Because of the factor of  $n!$  that appears in Eq. (4.1), a plot of  $\alpha_n$  vs  $n$  does not give an exponential law of the form displayed in Eq. (1.1). It is for this reason we think that the proof offered by McGill *et al.* leads to conclusions that are not correct. Both examples we have investigated lead to results which contradict this conclusion. As we remarked in Sec. I, these authors have also calculated the intensity of the multiphonon absorption peaks for a set of independent oscillators, each of which is described by the Morse potential. Their calculation is carried out by a quantum-mechanical means, and yields a result in agreement with ours in the limit  $\hbar\omega_0 < k_B T$ , where

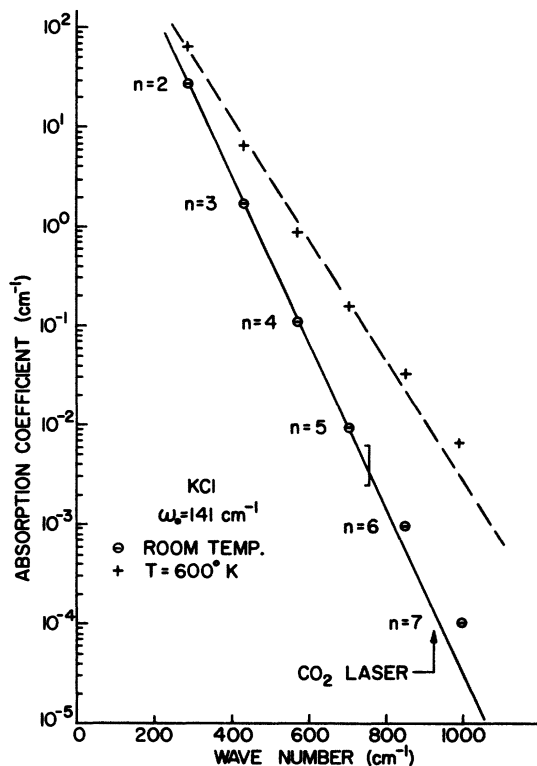


FIG. 1. Comparison between the multiphonon data in KCl and the noninteracting oscillator model, for the case where the motion of the oscillator is governed by the Morse potential. The solid line passes through the room-temperature data points of Deutsch and all the data lie to the left of the square bracket placed on the curve near  $750 \text{ cm}^{-1}$ . The barred circles are computed from the theoretical model, with parameters adjusted to fit the data at  $n=2$  and  $5$ . The crosses give the theoretical prediction when  $T=600^\circ\text{K}$ , and the dashed line is a straight line drawn as an aid to the eye.

the correspondence principle dictates that the classical and quantum-mechanical results must concur.

One must then inquire into the reason why the data are so well fitted by the exponential form displayed in Eq. (1.1). Of course, it may be that our independent oscillator model is so highly simplified that conclusions based on it are unreliable. We think that the problem does not lie here, but in the fact that the data obtained to date extend only over a rather small range of frequency, from  $2\omega_0$  to  $6\omega_0$  at best. The frequency only varies by a factor of at most 3 through this range. While the absorption coefficient changes by many decades as one passes through this frequency range, measurements over a wider range of frequencies, or at higher temperatures, will be required to determine whether the phenomenological form in Eq. (1.1) is valid.

We illustrate this point in Fig. 1, where we present the multiphonon absorption data obtained by Deutsch,<sup>2</sup> and compare it with the prediction of Eq. (4.1) at integral values of  $n\omega_0$ . The solid line in Fig. 1 is a straight line, chosen with slope such that it passes through the data obtained by Deutsch. We have omitted the data points simply to avoid cluttering the figure but, as noted by Deutsch, the data fall on the straight line. It will be important for our purposes to note that the data points all lie below the frequency of  $750 \text{ cm}^{-1}$ , to the left of the square bracket which has been placed on the straight line. Thus, the portion of the straight line to the right of this bracket represents an extrapolation of the data to higher frequencies, in particular to the frequency of the  $\text{CO}_2$  laser. This extrapolation assumes that the phenomenological form given in Eq. (1.1) is valid for all frequencies, since it is a linear extrapolation on a semilog plot.

In Fig. 1, the barred circles represent the prediction of Eq. (4.1). To place the points on the figure, we have adjusted  $\alpha_1$  and  $D$  so that Eq. (4.1) fits the data at the two points  $n=2$  and  $5$ . When we then calculate the strength of the absorption at  $n=3$  and  $4$ , we obtain results that agree very well with the data, to within the accuracy of the graph. Thus, we can also fit the function in Eq. (4.2) to the data, and it is clear that the measurements do not extend over a range of frequencies large enough to warrant the conclusion that the exponential law provides a unique description of the results.

It is not hard to see why we obtain a good fit to the data. The ratio  $k_B T/4D$  is quite small, of the order of  $10^{-2}$  typically, as we shall see shortly. If we plot the data on a semilog plot, then we are concerned with the behavior of  $\ln \alpha_n$  as a function of  $n$ . Equation (4.1) then gives

$$\ln \alpha_n = -n \left[ \ln \frac{4D}{k_B T} - \frac{1}{n} \ln n! \right] + \ln \left( \frac{4D \alpha_1}{k_B T} \right).$$

TABLE I. Morse potential parameters  $D$  and  $a$  required to fit the TO phonon frequency and multiphonon absorption data of Deutsch, for a series of alkali halides. Included is the (linear) thermal-expansion coefficient computed from the model for these crystals, along with measured values of the thermal-expansion coefficient, at room temperature.

Crystal	$D$ (units of $10^{-12}$ erg)	$a$ (in units of $10^8$ cm $^{-1}$ )	Calculated thermal expansion coefficient (units of $10^{-6}$ °K)	Measured thermal expansion coefficient (units of $10^{-6}$ °K)
NaCl	0.73	1.2	40	40
KCl	0.60	1.4	40	37
KBr	0.77	0.9	46	39
LiF	0.32	2.2	75	33

If  $n$  is large enough for Stirling's approximation to be used,  $\ln n! \approx n \ln n - n$  and

$$\ln \alpha_n = -n \left[ 1 + \ln \frac{4D}{k_B T} - \ln n \right] + \ln \left( \frac{4D \alpha_1}{k_B T} \right).$$

Since  $4D/k_B T \gg 1$ , the  $\ln(4D/k_B T)$  contribution to the quantity in square brackets is quite large. Furthermore, if we plot  $\ln \alpha_n$  as a function of  $n$ , deviations from a straight line arise only because of the  $\ln n$  term. Since  $\ln n$  is a slowly varying function of  $n$ , a plot of  $\ln \alpha_n$  vs  $n$  can give a result approximated very well by a straight line, if only a small range of  $n$  is examined.

If, for the moment, we accept the results of our independent oscillator model as realistic, then from Fig. 1 one can see that extrapolation of the exponential law in Eq. (1.1) to higher frequencies can lead to serious errors in estimates of the absorption coefficient. For example, by the time  $n=7$ , the expression in Eq. (4.1) gives a value of the absorption coefficient larger by a factor of 5 than that obtained from extrapolation of the exponential law. This example suggests that to estimate the absorption coefficient at  $10.6 \mu$  by the use of Eq. (1.1) to extrapolate data from lower frequencies may lead to a serious underestimation of the absorption coefficient at  $10.6 \mu$ .

If the temperature of the crystal is raised, the discussion above suggests that deviations from the near-exponential behavior should be expected to be more severe, and to set in at lower values of  $n$ . To illustrate this point, on Fig. 1 we have placed a series of crosses to represent the prediction of Eq. (4.1) at  $T=600$  °K, once  $\alpha_1$  and  $D$  have been adjusted to fit the room-temperature data at  $n=2$  and 5, as described above. The dashed line is a straight line placed on the graph as an aid to the eye. The deviations are indeed more pronounced, although on the semilog plot they do not look large if one adjusts the slope of the straight line to give the best fit.

In order to see if the independent oscillator model provides a fit to the data with realistic parameters, we have done the following for the case where the molecular potential is assumed to be

the Morse potential. We have determined the parameters of the Morse potential by the use of the value of the TO frequency, and the multiphonon data on the four alkali halide crystals studied by Deutsch.<sup>2</sup> When this information is combined with the tabulated value of the interatomic spacing, the coefficient of (linear) thermal expansion may be calculated for the model. We shall describe the details of the analysis below. The results of the investigation are summarized in Table I. For NaCl, KCl, and KBr, this procedure gives results in remarkable accord with measured values of the thermal expansion coefficient. For LiF, the agreement is poorer, but the estimated and measured value of the thermal-expansion coefficient still differs by little more than a factor of 2. On the basis of this analysis, we conclude that multiphonon absorption processes of an intrinsic character are indeed responsible for the absorption measured by Deutsch.

To obtain the numbers displayed in Table I, we have employed the following procedure. From Eq. (3.14), one sees that the slope of a plot of  $\ln \alpha_n$  vs  $n$  is controlled only by the parameter  $D$ , for the Morse potential. We have obtained the value of  $D$  given in Table I by fitting the ratio  $\alpha_5/\alpha_2$  to the data of Deutsch. The value of  $a$  is obtained by identifying the frequency  $\omega_0$  [Eq. (3.3)] with the TO phonon frequency of the crystal. The parameter  $x_0$  in the Morse potential is chosen to be equal to the nearest-neighbor interatomic spacing in the crystal.

In the quasiharmonic region, where  $k_B T \ll D$ , it is an elementary matter to calculate the mean value  $\langle x \rangle$  of the interatomic separation of the two atoms in the molecule. One finds

$$\langle x \rangle = x_0 + 3k_B T / 4aD,$$

where the second term is small compared to  $x_0$ . We identify the coefficient of (linear) thermal expansions with the ratio  $\delta \langle x \rangle / x_0 \delta T$ , where  $\delta \langle x \rangle$  is the change in the mean separation of the atoms produced by the temperature change  $\delta T$ . If we call  $\beta_T$  the expansion coefficient, then

$$\beta_T = 3k_B / 4aDx_0. \quad (4.2)$$

The figures in the third column of Table I have been obtained from Eq. (4.2), and in the right-hand column we give the experimental data.<sup>8</sup>

One intriguing feature of the results of Sec. III is that the strength of the  $n$ -phonon absorption peak for the Morse potential, and for the potential  $bx^2 + a/x^2$ , exhibits nearly the same functional dependence on  $n$ . This leads one to expect that the result in Eq. (4.1) may be rather general in the limit of large  $n$ , valid in the classical regime for any potential that admits an harmonic approximation, as long as the anharmonic corrections to the particle motion are small. At this time, we have not succeeded in providing a general proof of this result, however.

We conclude this section with some comments about the possible role impurities may play in affecting the behavior of the absorption coefficient at high frequencies. If the impurities are coupled to the ions of the host lattice by means of an interaction that may be crudely represented by either the Morse potential or the potential  $bx^2 + a/x^2$ , then within the framework of our model, the impurities will not affect the qualitative behavior of the absorption coefficient. However, they will affect it in a quantitative sense, since a certain fraction of the lattice oscillators will then be described by parameters that differ from the oscillators that describe the host lattice.

However, there are certain impurity ions that behave in an anomalous manner when present as substitutional impurities in alkali halides. An example is the  $\text{Li}^+$  ion, which frequently gives rise to a very-low-frequency-resonance phonon mode, even though it is a very light ion which would produce a high-frequency local phonon mode if it is coupled to the host ions by interactions characterized by harmonic force constants comparable to those in the host matrix. Evidently in the case of  $\text{Li}^+$ , in the harmonic approximation the force constants are very much smaller than those which characterize the host, small enough to offset the tendency of the light mass to create a high-frequency local mode. In fact, in KCl the  $\text{Li}^+$  ion sits off the substitutional lattice site, in the [111] direction; while it sits on site in KBr. These facts suggest that the  $\text{Li}^+$  ion moves in a potential well with a rather flat bottom, while terms higher order than quadratic in the displacement of the  $\text{Li}^+$  ion from the substitutional site play an important role in the lattice potential energy. This notion is supported by theoretical studies<sup>9</sup> and by experimental observations, which show very large electric-field-induced shifts in the frequency of the resonance mode.<sup>10</sup> It is also true that a number of other ions have been observed to produce resonance modes with frequencies very much lower than the frequency expected on the basis of mass-defect con-

siderations alone.<sup>10</sup>

The remarks of the preceding paragraph indicate that there are a certain number of impurities that, when placed in alkali halides, may be crudely described as moving in the cage formed by their nearest neighbors, with the floor of the cage quite flat in character. The calculation presented in Sec. III of the contribution to the absorption coefficient from the particle in the square well suggests that these impurities may give a contribution to the absorption coefficient that falls off as  $\omega^{-2}$  for frequencies large compared to the resonance frequency  $\omega_T$  at which the peak in the impurity-induced absorption occurs. Thus, the presence of a significant number of impurities that give rise to very-low-frequency resonances may have a significant qualitative effect on the behavior of the high-frequency absorption coefficient.

Before we proceed to an estimate of the quantitative effect of these impurities on the absorption coefficient near  $10.6 \mu$ , we first note that for typical values of parameters, the characteristic frequency  $\omega_T$  in the discussion of Sec. IIIC indeed lies in the proper spectral region. For example, if  $L = 3 \times 10^{-8}$  cm and if  $m$  is chosen to be 50 a. u., then  $\omega_T \approx 15 \text{ cm}^{-1}$ , a frequency in the spectral region where the low-lying impurity-induced lattice resonances are observed. Also, the resonance-mode frequency in some cases is observed to increase significantly with temperatures. Of course, we cannot expect our very crude model to account for the features of these resonance modes in a systematic and complete manner, but the over-all qualitative features seem to be reasonable.

It is a straightforward matter to find an expression for the contribution of  $N_I$  impurities to the absorption coefficient, in the limit  $\omega \gg \omega_T$ . This may be done by multiplying Eq. (3.45) by  $N_I$ , the number of impurities in the sample, dividing the result by the (time-averaged) energy stored in the electromagnetic field ( $\epsilon_\infty V E_0^2 / 8\pi$ , where  $\epsilon_\infty$  is the optical dielectric constant and  $V$  the crystal volume), then multiplying this by  $\epsilon_\infty^{1/2} / c$  to obtain  $1/L$ , where  $L$  is the distance required for the energy density of the wave to decay to  $1/e$  of its initial value. One finds

$$\frac{1}{L} = 16\pi^{1/2} f \frac{nq^2}{m} \frac{1}{c\epsilon_\infty^{1/2}} \frac{\omega_T}{\omega^2}, \quad (4.3)$$

where  $n = N/V$  is the number of unit cells per unit volume of the host crystal and  $f$  is the impurity concentration. In Eq. (4.3),  $q$  and  $m$  are the effective charge and mass of the impurity. Let  $q_0$  and  $m_0$  be the effective charge and reduced mass of the unit cell in the host crystal, and let

$$R = \frac{q^2}{q_0^2} \frac{m_0}{m}. \quad (4.4)$$

Then Eq. (4.3) may be written

$$\frac{1}{L} = \frac{4}{\pi^{1/2}} R \left( \frac{\epsilon_s - \epsilon_\infty}{\epsilon_\infty^{1/2}} \right) f \left( \frac{\omega_0}{\omega} \right)^2 \frac{\omega_T}{c}, \quad (4.5)$$

where  $\epsilon_s = \epsilon_\infty + 4\pi n^2 q_0^2 / m_0 \omega_0^2$  is the static dielectric constant of the host.

For the purposes of providing a crude estimate of the sensitivity of the absorption coefficient at  $10.6 \mu$  to the presence of these anomalous impurities, we set  $R$  and  $(\epsilon_s - \epsilon_\infty) / \epsilon_\infty^{1/2}$  equal to unity, and suppose  $\omega / \omega_0 \sim 7$  and  $\omega_T = 20 \text{ cm}^{-1}$ . We then find

$$1/L \approx 5f (\text{cm}^{-1}), \quad (4.6)$$

where  $f$  is the impurity concentration.

The quantitative estimate of  $L$  displayed in Eq. (4.6) must be regarded as extremely crude, because the model is highly oversimplified. It does suggest that near  $10.6 \mu$ , the absorption coefficient of the crystal may be quite sensitive to small concentrations of Li, Ag, Cu, or other impurities which give rise to impurity-induced resonance modes with frequency very much lower than expected on mass defect considerations. It would be extremely interesting to measure the effect on the absorption coefficient of doping KCl with Li, with concentrations in the range of 0.1 at. % to test this conjecture.

\*Research supported by The Advanced Research Projects Agency of The Department of Defense and monitored by The Defense Supply Service, Washington, D. C. under Contract No. DAHC 15-72-C-0129.

<sup>1</sup>For a discussion of the fundamental physical concepts employed in this area, we refer the reader to M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford U. P., London, 1954).

<sup>2</sup>T. F. Deutsch (unpublished).

<sup>3</sup>T. C. McGill, R. W. Hellwarth, M. Mangir, and H. V. Winston, report of work prior to publication.

<sup>4</sup>H. S. Heaps and G. Herzberg, *Z. Phys.* **133**, 48 (1952).

<sup>4a</sup>M. Sparks and L. J. Sham, *Solid State Commun.* **11**, 1451 (1972).

<sup>5</sup>See the discussion in *Mechanics* (Pergamon, Oxford, England, 1969), Chap. III.

<sup>6</sup>I. S. Gradshteyn and I. M. Ryzik, *Table of Integrals, Series and Products* (Academic, New York, 1965).

<sup>7</sup>W. Gröbner and N. Hofreiter, *Integraltafel* (Springer-Verlag, Vienna, 1950), Vol. II, p. 115.

<sup>8</sup>The experimental data have been taken from the tabulations in *American Institute of Physics Handbook*, edited by Dwight E. Gray (McGraw-Hill, New York, 1972), pp. 4-137 and 4-138.

<sup>9</sup>R. J. Quigley and T. P. Das, *Phys. Rev.* **164**, 1185 (1967); *Phys. Rev.* **177**, 1340 (1969).

<sup>10</sup>For a rather complete discussion of the properties of a number of impurities in alkali halides which give rise to low-lying lattice resonance modes, see B. P. Clayman, R. D. Kirby, and A. J. Sievers, *Phys. Rev. B* **3**, 1351 (1971).

## Raman Scattering in Small Crystals

T. P. Martin and L. Genzel

*Max-Planck-Institut für Festkörperforschung, Stuttgart, Germany*

(Received 6 March 1973)

The Raman scattering of a powder composed of small crystals of a noncentrosymmetric ionic material is considered using the Nyquist-theorem approach of Barker and Loudon. For modes that are both Raman and infrared active, the splitting of the transverse- and longitudinal-phonon frequencies is determined by the local electric field. This local field depends on the shape of the particles and on the powder density. The relative contribution to the Raman scattering from macroscopic electric field fluctuations and from atomic displacement fluctuations is also dependent on the powder density. This effect yields an antiresonance in the Raman intensity scattered by longitudinal phonons.

### I. INTRODUCTION

It has been established experimentally that the frequencies of infrared-active modes of vibration can be dependent on the size and shape of the crystal measured.<sup>1</sup> If the crystal is small enough to make an electrostatic approximation, this effect can be attributed to a change in the local field in a unit cell due to the surface depolarization charge.<sup>2</sup> The local field influences the long-wavelength

characteristic frequencies. This simplest of descriptions would be applicable to an absorption experiment performed on one crystal with dimensions on the order of  $1 \mu\text{m}$ . The optical-phonon frequency in such a sample would be shape dependent and size independent. It is, of course, not convenient to make optical measurements on only one crystal of microscopic dimensions. The local field in more convenient samples, composed of many small crystals, is additionally influenced by