Explicit exponential frequency dependence of multiphonon infrared absorption*

L. J. Sham

University of California, San Diego, La Jolla, California 92037[†]
Xonics, Inc., Van Nuys, California 91406

M. Sparks

Xonics, Inc., Van Nuys, California 91406
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The nearly exponential frequency dependence of the infrared absorption coefficient β observed by Rupprecht, Deutsch, and others has been explained previously by evaluating the individual n-phonon contributions to β, summing the results, and noting that the sum was nearly exponential over a fairly wide range of frequencies. A new derivation of the multiphonon absorption coefficient yields $\beta \sim e^{-\omega \tau}$ directly, rather than as a sum on n, and provides a prescription for estimating the range of ω over which the nearly exponential behavior extends.

The nearly exponential frequency dependence of the infrared absorption coefficient β observed[1] in LiF, NaF, NaCl, KCl, KBr, MgF_2, CaF_2, BaF_2, SrF_2, MgO, Al_2O_3, SiO_2, TiO_2, $BaTiO_2$, and $SrTiO_2$ has been explained by a theory of multiphonon absorption in which the individual n-phonon processes were calculated, summed, and the sum observed to be a nearly exponentially decaying function of frequency ω. Since this frequency dependence of β has attracted wide attention, a derivation of the exponential dependence in closed form, rather than as a sum over the individual n-phonon contributions, is of interest. A brief description of the results was presented elsewhere[2] in connection with the temperature dependence of β.

This derivation is accomplished as follows: First, our previous approximation[3,4] of using the central-limit theorem to reduce the multiple sum over phonon coordinates to a Gaussian is not made. Rather, using a well-known integral representation of the energy-conserving δ function reduces the previous expression for β to a time integral of a sum over n. This infinite sum on n is expressed as a sum of a few simple functions, which are easily integrated to give the closed-form exponential. The details are as follows.

The previous formal expression for β is[3,4]

$\beta = \sum_{n=2}^{\infty} \beta_n$ with

$$\beta_n = (\text{const}) f(\omega) \omega^{-4} (\Lambda_n^2 / n \, !)$$

$$\times \sum_{Q_1} \circ \circ \cdot \sum_{Q_n} \delta \left(\omega - \sum_{j=1}^{n} \omega_{Q_j} \right) \prod_{l=1}^{n} \sigma_{Q_l} , \qquad (1)$$

where $f(\omega) = 1 - e^{-\omega / \omega_T}$ is very nearly independent of the laser frequency ω for most cases of interest,

$$\omega_T = k_B T / \hbar,$$

$$\sigma_{Q_l} = W_{Q_l} (n_{Q_l} + 1) N \omega_p / \omega_{Q_l} ,$$

$$\omega_p = \hbar / 2 \rho_K^2 m ,$$

m is the reduced mass, ρ_K is the damping length in the Born-Mayer potential, W_{Q_l} is a dimensionless constant that is of order unity for large ω_{Q_l} and is very small for small ω_{Q_l}, n_{Q_l} are phonon occupation numbers, $2N$ is the number of ions in the crystal, and the higher-order terms in the perturbation expansion give rise to the vertex-correction factors

$$\Lambda_n = 1 + A_n \xi + O(\xi^2), \qquad A_n = \sum_{m=2}^{n-1} \binom{n}{m} m^{-2} , \qquad (2)$$

where $A_4 = 1.94$, $A_5 = 3.93$, $A_6 = 7.15$, $A_7 = 12.36$, and

$$\xi \cong 9 B_0 a_0 / 5 (1 - 2\rho_0) m \omega_m^2 .$$

Here B is the bulk modulus, $\rho \equiv \rho_K / a$, the subscript 0 denotes $T = 0$, and ω_m is a frequency near the top of the phonon spectrum. Equation (1) can be written down immediately from the well-known expression[3–5] for β with $\omega^2 \gg \omega_f^2$ (ω_f is the reststrahl frequency) and standard perturbation-theory results, apart from the details of Λ_n and W_{Q_l} which are not needed here. In the previous calculation,[3,4] the central-limit approximation was used to reduce the n-fold multiple sum over $Q_1 \cdots Q_n$ in Eq. (1) to a Gaussian whose position, height, and width are given by single sums over phonon coordinates. The sum of these Gaussians then gave a nearly exponential frequency dependence of β.

Representing $\delta(\omega - \sum \omega_{Q_j})$ by

$$(2\pi)^{-1} \int dt \, e^{i\omega t} \prod_j \exp(-i\omega_{Q_j} t)$$

and using the approximation

$$\Lambda_n^2 / n^4 n \, ! \cong D^n , \qquad (3)$$

reduces (1) to

$$\beta = [f(\omega) / 2\pi \omega^4] \int_{-\infty}^{\infty} dt \, e^{i\omega t} \sum_{n=2}^{\infty} n^4 [g(t)]^n , \qquad (4)$$

where $g(t) = D \sum_Q \sigma_Q e^{-i\omega_Q t}$. The value of D and the range of n over which (3) is valid are obtained by

plotting $\ln(\Lambda_n^2/n^2 n!)$ as a function of n as discussed below.

In order to illustrate the central features of the calculation as simply as possible, we first approximate ω^4 by $n^4\bar{\omega}^4$, where $\bar{\omega}$ is an average frequency having a typical value $\bar{\omega} \cong \omega_f$. Physically, the phonon driven at frequency ω decays into n phonons whose average frequency is $\bar{\omega}$. The resulting sum in (4) can be written

$$\sum_{n=2}^{\infty} g^n = (1-g)^{-1} - 1 - g.$$

When this expression is substituted into (4), the term

$$(2\pi)^{-1} \int dt\, e^{i\omega t}(1+g)$$

$$= \delta(\omega) + N^{-1}\sum_Q W_Q(n_Q + 1)n_Q^{-1}\delta(\omega_Q - \omega)$$

vanishes for $\omega > \omega_g$, where ω_g is the greatest phonon frequency. Evaluating the remaining integral

$$\int dt\, e^{i\omega t}(1-g)^{-1},$$

which has a simple pole at $t = i\tau$, where τ is the solution to $1 - g(i\tau) = 0$, gives

$$\beta = \beta_0 e^{-\tau \omega},$$

$$\beta_0 = (\text{const})f(\omega)\left(\bar{\omega}^4 \frac{dg(i\tau)}{d\tau}\right)^{-1}. \qquad (5)$$

The equation for τ,

$$1 - D\omega_p N^{-1}\sum_Q W_Q(n_Q + 1)\omega_Q^{-1} e^{\omega_Q \tau} = 0, \qquad (6)$$

is easily solved numerically for specific cases.[6] The following approximate solution illustrates the general dependence of τ on T, Λ_n, etc., although it is too crude to afford accurate values of τ. Neglecting the angle dependence of W_Q and using the Einstein approximation $\delta(\omega - \omega_E)$ to the density of states gives

$$\tau \cong -\omega_E^{-1} \ln[6D\omega_p W_E(n_E + 1)/\omega_E], \qquad (7)$$

$dg(i\tau)/d\tau = \omega_E$. Making these approximations to determine the value of τ is more reasonable than making the same approximation in (1). The latter gives β as a sum of δ functions. For NaCl at 300 K with $\omega_E = \omega_f$, Eq. (7) gives $\omega_f\tau = 3.4$, in fortuitously good agreement with the experimental value of 3.2 in view of the crudeness of the approximate solution (7). Other simple approximate solutions to (6) can be obtained. For example, neglecting the angle dependence of W_Q, using the truncated Debye approximation

$$\Theta(\omega - \tfrac{1}{2}\omega_D)\Theta(\omega_D - \omega)3\omega_Q^2/\omega_D^3$$

to the density of states (where the truncation at $\frac{1}{2}\omega_D$ accounts for the fact that W_Q is small for small ω_Q[3,4]), making the high-temperature approx-

imation $n_Q + 1 \cong \hbar\omega_Q/k_B T$, and reinserting $\hbar\omega_D/k_B T \cong n_{\omega_D} + 1$ after integration gives

$$\tau \cong -\omega_D^{-1} \ln[6D\omega_p W_b(n_{\omega_D} + 1)/\omega_D]$$

$$+ \omega_D^{-1} \ln(\tfrac{1}{3}\omega_D \tau), \qquad (8)$$

which is quite similar to (7), since the last term in (8) is small, the value of $\omega_D \tau$ being approximately equal to 3 for typical cases.

It is not necessary to make the approximation $\omega = n\bar{\omega}$. The sum in (4) can be written

$$\sum_{n=0}^{\infty} n^4 g^n = \left(g \frac{\partial}{\partial g}\right)^4 \frac{1}{1-g} = \frac{4!}{(1-g)^5} - \frac{10(3!)}{(1-g)^4}$$

$$+ \frac{25(2!)}{(1-g)^3} - \frac{15}{(1-g)^2} + \frac{1}{1-g}. \qquad (9)$$

Each integral is evaluated by residues, which gives (5) as the leading term, with the same value of τ as before, but with

$$\beta_0 = (\text{const})f(\omega)\left(\frac{dg(i\tau)}{d\tau}\right)^{-5}. \qquad (10)$$

For the Einstein approximation above, the new value of β_0 is $(\text{const})f(\omega)/\omega_E^5$, which is quite similar to the previous value $\beta_0 = (\text{const})f(\omega)/\bar{\omega}^4\omega_E$. (If the Einstein approximation is made in evaluating $\bar{\omega}$ also, then $\bar{\omega} = \omega_E$, and the two results are identical.) The small correction terms to (10), which vanish in the limit of the single-frequency approximation discussed above, can be obtained simply in terms of cumulent moments by carrying out the straightforward details of the calculation outlined above. In this calculation, the results (9) and

$$n^4 = [(n+4)! - 10(n+3)! + 25(n+2)! - 15(n+1)!$$

$$+ n!]/n!$$

are useful.

It was clear from our previous analysis[3,4] that the nearly exponential dependence of β would be valid only over a limited range of frequency. The present results make it even simpler to study this range of validity. Two features of the exponential are of interest—the over-all near-exponential decay, which could show local structure such as multiphonon peaks superimposed on the decay, and the smoothness (presence or lack of multiphonon peaks) of the $\beta(\omega)$ curves. The latter has been discussed previously.[3,4] Briefly, the smoothness of the phonon density of states, the phonon lifetimes, the broadening of any structure with each convolution involved in going from β_n to β_{n+1}, and the ratio of the width to the spacing of the Gaussians obtained in applying the central-limit theorem are important in determining the smoothness of $\beta(\omega)$.

An over-all exponential behavior is obtained when (i) $\Lambda_n^2/n^4 n!$ is an exponential function of n, that is,
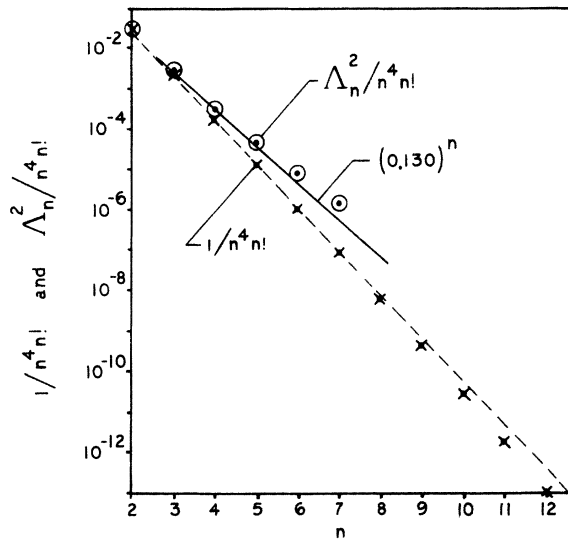
FIG. 1. Values of $1/n^4 n!$ and $\Lambda_n^2/n^4 n!$ used in determining the range over which β decays exponentially with increasing frequency. The values of Λ_n^2 are for NaCl at 300 K, for which $\xi = 0.18$. The straight line is fit to the $1/n^4 n!$ points at small n.

(3) is satisfied; and (ii) $f(\omega)$ is essentially independent of ω. The second condition is satisfied for most cases of interest. For example, $\omega_T = 208$ cm^{-1} at 300 K, and $\omega_f = 164$ cm^{-1} for NaCl at 300 K; thus $f(\omega) \cong 1 - e^{-164 n/208} \cong 1$ for $\omega = n\omega_f$ with $n \gtrsim 2$. However, for small ω and high T, $f(\omega)$ does become a nonconstant function of ω. Concerning (i),

the function $\ln(1/n^4 n!)$ is nearly linear in n over a large range of values for n, while $\ln(\Lambda_n^2/n^4 n!)$ has a positive curvature as seen in Fig. 1. Over a limited range of n, which often includes the experimental values, $\Lambda_n^2/n^4 n!$ is nearly exponential in n; consequently, β is nearly exponential in ω. For example, in Fig. 1, $\ln(\Lambda_n^2/n^4 n!)$ is well approximated by the straight line D^n with $D = 0.130$ for $n = 3$–5, which is the experimental range over which the nearly exponential frequency dependence was observed.

The vertex-correction factor Λ_n^2 causes $\Lambda_n^2/n^4 n!$ to deviate above the exponential as n increases. (The corresponding increase of β above the exponential as ω is increased is not as drastic as that of $\Lambda_n^2/n^4 n!$ since β contains an explicit exponential dependence in addition to the nearly exponential term $\Lambda_n^2/n^4 n!$.) Thus, larger values of ξ give greater deviation from the exponential. The oversimplified model of Ref. 7 takes $\xi = 1$, which greatly overestimates the vertex correction and gives noticeable deviations of β from the exponential even over the small range of experimental values of n. Our estimate of $\xi = 0.18$ may even be too large.[3,8]

The recently observed[8] deviation of the T dependence of β from the previously expected results has been explained[2] by including the T dependence of the phonon frequencies and lattice constants in our previous theory. The present result displays the temperature dependence in a much simpler form, the T dependence being contained in the two parameters β_0 and τ.

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