

RAMAN SCATTERING OF ATOMIC VIBRATIONS IN ANHARMONIC POTENTIALS

PETER KNOLL

*Institut für Experimentalphysik, Universität Graz, Universitätsplatz 5
A-8010 Graz, Austria*

and

CLAUDIA AMBROSCH-DRAXL

*Institut für Theoretische Physik, Universität Graz, Universitätsplatz 5
A-8010 Graz, Austria*

ABSTRACT

A formalism for calculating Raman spectra of anharmonic vibrations is developed using vibrational matrix-elements and the complex dielectric function which can be achieved from ab-initio band-structure methods. This procedure can be applied to systems ranging from molecules to solids.

1. Introduction

Raman scattering allows to get useful information about the vibrational behavior of molecules as well as of solids. Anharmonic effects can be observed in overtones and line-shapes and in their temperature dependence. Whereas the Raman spectrum directly reflects the anharmonicity of molecular vibrations, the situation is much more complicated in a crystal, because a large number of elementary cells are coupled in a complex way. We have developed a method which takes into account the anharmonicity of the lattice-dynamical potential, where effects from phonon-phonon interaction within one phonon-branch are allowed. Thus the model is able to describe different systems from molecules to solids.

The aim of our method is to calculate Raman spectra from observables which can be directly obtained from frozen-phonon ab-initio band-structure calculations. These calculated quantities are the total energy per unit cell and the complex dielectric tensor, both as a function of the arrangement of the atoms within the unit cell.

A theoretical analysis of phononic Raman scattering in crystals has been given by several authors^{1,2,3}. We develop the description of phononic scattering compatible with the ab-initio formalism. In the following section we express the Raman intensity by fluctuations of the dielectric function. In Section 3 the expectation values of phononic properties will be extracted from the anharmonic frozen-phonon potential. Following this procedure we obtain a quantitative calculation of Raman spectra including anharmonic atomic potentials, temperature effects and their dependence on the coherence length (cluster size). An application to the O(4)-vibration in YBa₂Cu₃O₇ is given by Ambrosch-Draxl et al.⁴ in this volume.

2. Raman scattering in crystals

The simplest way to establish the relation between the scattered radiation and the dielectric function is to study the scattered radiation field at a long distance R with the polarization vector \vec{e}_s according to an oscillating dipole-moment represented by its second derivative $\ddot{\vec{p}}_s(t)$.

$$E_s \left(t + \frac{R}{c} \right) = \frac{1}{4\pi\epsilon_0 c^2 R} \vec{e}_s \ddot{\vec{p}}_s(t) \quad (1)$$

ϵ_0 and c are the permittivity and the velocity of light, respectively. Within one unit cell with volume V_E the α component of the dipole-moment \vec{p}_s induced by the β component of the applied laser field E_L with the polarization vector \vec{e}_L is

$$p_s^\alpha(t) = V_E \epsilon_0 \left(\epsilon^{\alpha\beta}(t) - \delta^{\alpha\beta} \right) E_L(t) e_L^\beta, \quad (2)$$

where $\epsilon^{\alpha\beta}(t)$ is the complex dielectric tensor.

Time fluctuations in the dielectric function cause inelastic scattering. In that case the non-fluctuating part $\delta^{\alpha\beta}$ (Kronecker symbol) does not contribute. If we take the ω_s Fourier component indicated by the brackets $[]_{\omega_s}$ we can express the second derivative of the oscillating dipole-moment at frequency ω_s for one elementary cell:

$$\ddot{p}_s^\alpha(t) = V_E \epsilon_0 \omega_s^2 \left[\epsilon^{\alpha\beta}(t) E_L(t) e_L^\beta \right]_{\omega_s} \quad (3)$$

The time-fluctuations of the dielectric function at the incident laser frequency ω_L can be expanded into a Fourier series. We also have to consider that E_L , $\epsilon^{\alpha\beta}$, and E_s depend on space (represented by the corresponding space Fourier components) and we obtain the scattered radiation field E_s for one elementary cell at position \vec{r}_l :

$$E_s \left(\omega_s \left(t + \frac{R}{c} \right), \vec{k}_s (\vec{R} - \vec{r}_l) \right) = \frac{V_E \omega_s^2}{4\pi c^2 R} \left[\sum_{\omega, \vec{k}} e_s^\alpha \epsilon_{\omega_L}^{\alpha\beta}(\omega t, \vec{k} \vec{r}_l) e_L^\beta E_L(\omega_L t, \vec{k}_L \vec{r}_l) \right]_{\omega_s} \quad (4)$$

Fluctuations in time and space of the dielectric function are considered by the Fourier components ω and \vec{k} which may be independent, so far. If one considers that these fluctuations are caused by quasi-particle excitations of the solid, ω and \vec{k} are related by the dispersion relation $\omega(\vec{k})$ of the quasi-particle. In the same way the frequencies ω_L and ω_s and the wavevectors \vec{k}_L and \vec{k}_s of laser and scattered radiation, respectively, are related. The long time average of Equ. 4 directly results in the energy conservation $\omega_s = \omega_L \pm \omega$. Since, in a solid, the quasi-particle (e.g. a phonon) has a coherence volume consisting of N elementary cells (with volume V_E), we have to sum the scattered radiation field E_s over these N cells because they all contribute in a certain phase relation. This is performed by integrating \vec{r}_l over the coherence volume NV_E and gives in the limit $N \rightarrow \infty$ the known momentum conservation. In that case

($\vec{k}_s = \vec{k}_L \pm \vec{k}$) we obtain even for finite N :

$$E_{s, \vec{k}_s} \left(\omega_s \left(t + \frac{R}{c} \right) \right) = \frac{NV_E \omega_s^2}{4\pi c^2 R} \left[\sum_{\omega(\vec{k})} e_s^\alpha \varepsilon_{\omega_L}^{\alpha\beta} (\omega_{\vec{k}} t) e_L^\beta E_{L, \vec{k}_L} (\omega_L t) \right]_{\omega_s} \quad (5)$$

The indices \vec{k}_s , \vec{k}_L and \vec{k} indicate that each quantity has a specific wave-vector obeying the momentum conservation. In the following we will neglect these indices for simplicity. Using the time average indicated by the brackets $\langle \rangle$ and the relation

$$dP_s = c\varepsilon_0 \langle E_s, E_s^* \rangle R^2 d\Omega \quad (6)$$

the scattered power dP_s per solid angle $d\Omega$ is obtained for the scattering volume V_s :

$$\frac{dP_s}{d\Omega} = \frac{V_s NV_E \varepsilon_0 \omega_s^4}{(4\pi)^2 c^3} \left\langle \sum_{\omega(\vec{k})} e_s^\alpha \varepsilon_{\omega_L}^{\alpha\beta} (\omega_{\vec{k}} t) e_L^\beta E_L (\omega_L t), \sum_{\omega(\vec{k})} e_s^\alpha \varepsilon_{\omega_L}^{\alpha\beta*} (\omega_{\vec{k}} t) e_L^\beta E_L^* (\omega_L t) \right\rangle_{\omega_s} \quad (7)$$

It is assumed that there are several coherence volumina NV_E in the scattering volume V_s incoherently contributing to the total scattered radiation. Therefore, the total scattered power is increased by the factor V_s/NV_E . The Raman efficiency S is defined with the help of the differential cross section $d\sigma/d\Omega$:

$$S = \frac{1}{V_s} \frac{d\sigma}{d\Omega} \quad (8)$$

Introducing the new quantity $e_L^\beta(\omega_L t)$ which is the normalized electric field containing the polarization and variations in time

$$e_L^\beta E_L (\omega_L t) = |E_L| e_L^\beta (\omega_L t) \quad (9)$$

and using the relation between differential cross section, power and laser intensity I_L

$$\frac{dP_s}{d\Omega} = \frac{d\sigma}{d\Omega} \frac{\omega_s}{\omega_L} I_L \quad (10)$$

$$I_L = c\varepsilon_0 |E_L|^2 \langle e_L^\beta (\omega_L t), e_L^{\beta*} (\omega_L t) \rangle \quad (11)$$

we finally obtain

$$S(\omega_s) = \frac{NV_E \omega_L \omega_s^3}{(4\pi)^2 c^4} \frac{\left\langle \sum_{\omega(\vec{k})} e_s^\alpha \varepsilon_{\omega_L}^{\alpha\beta} (\omega_{\vec{k}} t) e_L^\beta (\omega_L t), \sum_{\omega(\vec{k})} e_s^\alpha \varepsilon_{\omega_L}^{\alpha\beta*} (\omega_{\vec{k}} t) e_L^{\beta*} (\omega_L t) \right\rangle_{\omega_s}}{\langle e_L^\beta (\omega_L t), e_L^{\beta*} (\omega_L t) \rangle} \quad (12)$$

or in other notation³

$$S_{\omega_s}^{\alpha\beta} = \frac{NV_E \omega_L \omega_s^3}{(4\pi)^2 c^4} \langle \delta\varepsilon^{\alpha\beta}, \delta\varepsilon^{\alpha\beta*} \rangle_{\omega_s}. \quad (13)$$

If the time fluctuations of the dielectric tensor are caused by phonons they can be described classically by the derivative of the dielectric tensor with respect to the phononic normal coordinate $\partial\varepsilon^{\alpha\beta}/\partial Q_{\omega_{\vec{k}_L}}$ and the phonon amplitude $Q_{\omega_{\vec{k}}}$. The time average of the ω_s Fourier component of the scattered light intensity normalized to the time averaged laser intensity is given in the classical limit by

$$\langle \delta\varepsilon^{\alpha\beta}, \delta\varepsilon^{\alpha\beta*} \rangle_{\omega_s} = \left[\frac{1}{2} \frac{\partial\varepsilon^{\alpha\beta}(\omega_L, \vec{k}_L)}{\partial Q_{\omega_{\vec{k}_L}}} Q_{\omega_{\vec{k}}}^0 \right]_{\omega_s=\omega_L \pm \omega}^2 \quad (14)$$

which is known to fail giving the correct intensity ratio between Stokes ($\omega_s = \omega_L - \omega$) and anti-Stokes scattering ($\omega_s = \omega_L + \omega$). One has to consider that Equ. 13 only expresses some general relation between the fluctuations in the dielectric function and the Raman efficiency. This holds for a classical as well as for a quantum–mechanical treatment. Using Equ. 13 the quantum–mechanical expression for Raman scattering is obtained by calculating the expectation value of the fluctuations in the dielectric function caused by some transitions between eigenstates $|i\rangle \rightarrow |f\rangle$:

$$\langle \delta\varepsilon^{\alpha\beta}, \delta\varepsilon^{\alpha\beta*} \rangle_{\omega_s} = \left| \left[\varepsilon_{i \rightarrow f}^{\alpha\beta} \right]_{\omega_s=\omega_L-\omega_{if}} \right|^2 \quad (15)$$

Using the expansion of the dielectric function $\varepsilon_{\omega_L}^{\alpha\beta}$ with respect to $Q_{\omega_{\vec{k}}}$

$$\begin{aligned} \varepsilon_{\omega_L}^{\alpha\beta}(Q_{\omega_{\vec{k}}}) &= \varepsilon_{\omega_L}^{\alpha\beta} \Big|_0 + \sum_{\omega(\vec{k})} \frac{\partial\varepsilon_{\omega_L}^{\alpha\beta}}{\partial Q_{\omega_{\vec{k}}}} \Big|_0 Q_{\omega_{\vec{k}}} + \frac{1}{2} \sum_{\omega(\vec{k})} \sum_{\omega'(\vec{k}')} \frac{\partial^2\varepsilon_{\omega_L}^{\alpha\beta}}{\partial Q_{\omega_{\vec{k}}} \partial Q_{\omega'_{\vec{k}'}}} \Big|_0 Q_{\omega_{\vec{k}}} Q_{\omega'_{\vec{k}'}} + \\ &+ \frac{1}{6} \sum_{\omega(\vec{k})} \sum_{\omega'(\vec{k}')} \sum_{\omega''(\vec{k}'')} \frac{\partial^3\varepsilon_{\omega_L}^{\alpha\beta}}{\partial Q_{\omega_{\vec{k}}} \partial Q_{\omega'_{\vec{k}'}} \partial Q_{\omega''_{\vec{k}''}}} \Big|_0 Q_{\omega_{\vec{k}}} Q_{\omega'_{\vec{k}'}} Q_{\omega''_{\vec{k}''}} + \dots \\ &+ \frac{1}{n!} \sum_{\omega(\vec{k})} \dots \sum_{\omega^{(n)}(\vec{k}^{(n)})} \frac{\partial^n \varepsilon_{\omega_L}^{\alpha\beta}}{\partial Q_{\omega_{\vec{k}}} \dots \partial Q_{\omega_{\vec{k}^{(n)}}}} \Big|_0 Q_{\omega_{\vec{k}}} \dots Q_{\omega_{\vec{k}^{(n)}}} \end{aligned} \quad (16)$$

the corresponding quantum–mechanical description can be found by introducing the appropriate operators:

$$\begin{aligned} \left[\varepsilon_{i \rightarrow f}^{\alpha\beta} \right]_{\omega_s} &= \langle f | \hat{\varepsilon}_{\omega_L}^{\alpha\beta} | i \rangle_{\omega_s=\omega_L-\omega_{if}} \\ &= \sum_n \frac{1}{n!} \sum_{\omega(\vec{k})} \dots \sum_{\omega^{(n)}(\vec{k}^{(n)})} \left\langle g \nu \left| \frac{\partial^n \hat{\varepsilon}_{\omega_L}^{\alpha\beta}}{\partial Q_{\omega_{\vec{k}}} \dots \partial Q_{\omega_{\vec{k}^{(n)}}}} \hat{Q}_{\omega_{\vec{k}}} \dots \hat{Q}_{\omega_{\vec{k}^{(n)}}} \right| g \mu \right\rangle_{\omega_s=\omega_L-\omega_{\mu\nu}} \\ &\sim \sum_n \frac{1}{n!} \sum_{\omega(\vec{k})} \dots \sum_{\omega^{(n)}(\vec{k}^{(n)})} \left\langle g \left| \frac{\partial^n \hat{\varepsilon}_{\omega_L}^{\alpha\beta}}{\partial Q_{\omega_{\vec{k}}} \dots \partial Q_{\omega_{\vec{k}^{(n)}}}} \right| g \right\rangle \left\langle \nu \left| \hat{Q}_{\omega_{\vec{k}}} \dots \hat{Q}_{\omega_{\vec{k}^{(n)}}} \right| \mu \right\rangle_{\omega_s=\omega_L-\omega_{\mu\nu}} \\ &\sim \sum_n \frac{1}{n!} \sum_{\omega(\vec{k})} \dots \sum_{\omega^{(n)}(\vec{k}^{(n)})} \frac{\partial^n \varepsilon_{\omega_L}^{\alpha\beta}}{\partial Q_{\omega_{\vec{k}}} \dots \partial Q_{\omega_{\vec{k}^{(n)}}}} \left\langle \nu \left| \hat{Q}_{\omega_{\vec{k}}} \dots \hat{Q}_{\omega_{\vec{k}^{(n)}}} \right| \mu \right\rangle_{\omega_s=\omega_L-\omega_{\mu\nu}} \end{aligned} \quad (17)$$

The transition frequency ω_{if} has to satisfy the relation $\omega_{if} = -\omega_{fi} = \omega$.

In order to achieve Equ. 17 we assume that the system can be divided into states $|\mu\rangle$ and $|\nu\rangle$ depending on the parameter Q and a state $|g\rangle$ with matrix elements independent of Q (Condon approximation). Thus the transition of the many-body eigenstates $|i\rangle$ to $|f\rangle$ only occurs in the phononic subsystem: $|i\rangle \rightarrow |f\rangle = |g\mu\rangle \rightarrow |g\nu\rangle$.

Although this assumption does not really require the Born–Oppenheimer approximation Born–Oppenheimer naturally satisfies it. As shown in Equ. 17 the matrix element can be split into two parts, an electronic one and a phononic one, which can be calculated separately.

Taking into account only one phononic branch $\omega(\vec{k})$ Equ. 17 can further be split into one-, two-, three-, four-phononic contributions, etc., all with total momentum transfer $\Delta\vec{k} = 0$ (as needed for light scattering in solids).

$$\begin{aligned}
[\varepsilon_{\mu \rightarrow \nu}^{\alpha\beta}]_{\omega_s}^{(1)} &= \frac{\partial \varepsilon_{\omega_L}^{\alpha\beta}}{\partial Q_0} \langle \nu | \hat{Q}_0 | \mu \rangle + \frac{1}{2} \frac{\partial^2 \varepsilon_{\omega_L}^{\alpha\beta}}{\partial Q_0^2} \langle \nu | \hat{Q}_0^2 | \mu \rangle + \frac{1}{6} \frac{\partial^3 \varepsilon_{\omega_L}^{\alpha\beta}}{\partial Q_0^3} \langle \nu | \hat{Q}_0^3 | \mu \rangle + \dots \\
[\varepsilon_{\mu \rightarrow \nu}^{\alpha\beta}]_{\omega_s}^{(2)} &= \sum_{\vec{k} \neq 0} \left\{ \frac{1}{2} \frac{\partial^2 \varepsilon_{\omega_L}^{\alpha\beta}}{\partial Q_{\vec{k}} \partial Q_{-\vec{k}}} \langle \nu | \hat{Q}_{\vec{k}} \hat{Q}_{-\vec{k}} | \mu \rangle + \frac{1}{24} \frac{\partial^4 \varepsilon_{\omega_L}^{\alpha\beta}}{\partial Q_{\vec{k}}^2 \partial Q_{-\vec{k}}^2} \langle \nu | \hat{Q}_{\vec{k}}^2 \hat{Q}_{-\vec{k}}^2 | \mu \rangle + \dots \right\} \\
[\varepsilon_{\mu \rightarrow \nu}^{\alpha\beta}]_{\omega_s}^{(3)} &= \sum'_{\vec{k}, \vec{k}'} \left\{ \frac{1}{6} \frac{\partial^3 \varepsilon_{\omega_L}^{\alpha\beta}}{\partial Q_{\vec{k}} \partial Q_{\vec{k}'} \partial Q_{-\vec{k}-\vec{k}'}} \langle \nu | \hat{Q}_{\vec{k}} \hat{Q}_{-\vec{k}} \hat{Q}_{-\vec{k}-\vec{k}'} | \mu \rangle + \dots \right\} \\
[\varepsilon_{\mu \rightarrow \nu}^{\alpha\beta}]_{\omega_s}^{(4)} &= \sum''_{\vec{k}, \vec{k}', \vec{k}''} \left\{ \frac{1}{24} \frac{\partial^4 \varepsilon_{\omega_L}^{\alpha\beta}}{\partial Q_{\vec{k}} \partial Q_{\vec{k}'} \partial Q_{\vec{k}''} \partial Q_{-\vec{k}-\vec{k}'-\vec{k}''}} \langle \nu | \hat{Q}_{\vec{k}} \hat{Q}_{\vec{k}'} \hat{Q}_{\vec{k}''} \hat{Q}_{-\vec{k}-\vec{k}'-\vec{k}''} | \mu \rangle + \dots \right\} \\
\dots \quad \text{etc.} & \quad \quad \quad (18)
\end{aligned}$$

Note that \sum' and \sum'' indicate that the sums do not include terms which already have been considered in the lower order processes.

As each of these processes contributes to the Raman intensity with different phase the complete Raman efficiency can be written as a thermal average of intensity contributions of all possible transitions:

$$S_{\omega_s}^{\alpha\beta} = \frac{NV_E \omega_L \omega_s^3 \sum_{\mu} e^{-E_{\mu}/kT} \sum_{\nu} \sum_n [\varepsilon_{\mu \rightarrow \nu}^{\alpha\beta}]_{\omega_s}^{(n)2}}{(4\pi)^2 c^4 \sum_{\mu} e^{-E_{\mu}/kT}} \quad (19)$$

This expression describes the integrated line intensity of the observed Raman spectrum. A direct simulation of the experiment can be achieved by

$$\frac{\partial S_{\omega_s=\omega_L-\omega}^{\alpha\beta}}{\partial \omega}(\omega) = \frac{NV_E (\omega_L - \omega)^3 \sum_{\mu} e^{-E_{\mu}/kT} \sum_{\nu} \sum_n [\varepsilon_{\mu \rightarrow \nu}^{\alpha\beta}]_{\omega_s}^{(n)2} L^{(n)}(\omega, \omega_{\mu\nu}, \gamma)}{(4\pi)^2 c^4 \sum_{\mu} e^{-E_{\mu}/kT}} \quad (20)$$

which represents a spectral density. The quantity $L^{(n)}$ can be a Lorentzian term for life-time broadening in one-phonon processes or it offers the opportunity to introduce an appropriate density of states for multi-phonon processes.

3. Determination of effective phononic potentials from ab-initio frozen-phonon calculations

Performing frozen-phonon ab-initio calculations the total energy per unit cell is obtained for each configuration of atoms within the unit cell. If one is interested in the properties of a specific phonon the atoms have to be displaced according to the normal coordinate $Q_{\omega_{\vec{k}}}$ of this vibration. We denote the corresponding displacement of atoms in the l -th elementary cell according to $Q_{\omega_{\vec{k}}}$ by $u_{l,\omega_{\vec{k}}}^i$. The index i runs over the three directions of all atoms in the elementary cell. The total movement of an atom in one direction is given by the usual Fourier sum over all phononic modes⁵:

$$u_l^i = \frac{1}{\sqrt{N}} \sum_{\omega_{\vec{k}}} \frac{e^{i\omega_{\vec{k}}}}{\sqrt{m_i}} Q_{\omega_{\vec{k}}} e^{i\vec{k}\vec{r}_l} = \sum_{\omega_{\vec{k}}} u_{l,\omega_{\vec{k}}}^i \quad (21)$$

The specific atomic displacement as used in the frozen-phonon calculations is then simply related to the phononic normal coordinate. Instead of plotting the total energy against the displacement of all atoms the one-dimensional quantity $u_{\omega_{\vec{k}}}$ is introduced. It is defined as the absolute value of the displacement vector of the atoms in one elementary cell:

$$u_{\omega_{\vec{k}}} = \sqrt{\sum_i |u_{l,\omega_{\vec{k}}}^i|^2} = \frac{1}{\sqrt{N f_{\omega_{\vec{k}}}}} Q_{\omega_{\vec{k}}} \quad (22)$$

The factor $f_{\omega_{\vec{k}}}$ includes the mass weight and the part of atomic movement in the specific normal coordinate:

$$1/f_{\omega_{\vec{k}}} = \sum_i \frac{e^{i\omega_{\vec{k}}}}{m_i} \quad (23)$$

In the special case of two moving atoms with mass m and $u_{l,\omega_{\vec{k}}}^1 = -u_{l,\omega_{\vec{k}}}^2$ (as it is the case for the O(4) vibration in YBa₂Cu₃O₇⁴) we can define in a similar way $u_{\omega_{\vec{k}}} = |u_{l,\omega_{\vec{k}}}^i|$ and obtain $f_{\omega_{\vec{k}}} = 2m$.

The total energy $V_{\omega_{\vec{k}}}$ per unit cell and the complex dielectric function can be expanded by $u_{\omega_{\vec{k}}}$. A fit of the ab-initio results determines the coefficients a_n and b_n of the following expressions:

$$\frac{V_{\omega_{\vec{k}}}(u_{\omega_{\vec{k}}})}{N} = a_0 + a_1 u_{\omega_{\vec{k}}} + a_2 u_{\omega_{\vec{k}}}^2 + a_3 u_{\omega_{\vec{k}}}^3 + a_4 u_{\omega_{\vec{k}}}^4 + \dots \quad (24)$$

$$\varepsilon_{\omega_L}^{\alpha\beta}(u_{\omega_{\vec{k}}}) = b_0 + b_1 u_{\omega_{\vec{k}}} + b_2 u_{\omega_{\vec{k}}}^2 + b_3 u_{\omega_{\vec{k}}}^3 + b_4 u_{\omega_{\vec{k}}}^4 + \dots \quad (25)$$

Using relation 22 the phononic potential is obtained:

$$\frac{V_k(Q_{\omega_{\vec{k}}})}{N} = a_0 + \frac{a_1}{(N f_{\omega_{\vec{k}}})^{1/2}} Q_{\omega_{\vec{k}}} + \frac{a_2}{N f_{\omega_{\vec{k}}}} Q_{\omega_{\vec{k}}}^2 + \frac{a_3}{(N f_{\omega_{\vec{k}}})^{3/2}} Q_{\omega_{\vec{k}}}^3 + \frac{a_4}{(N f_{\omega_{\vec{k}}})^2} Q_{\omega_{\vec{k}}}^4 + \dots \quad (26)$$

It is important to notice that for large N (solid state limit) only the second order term contributes (independently from N) and all higher order terms vanish. (a_0 can be set to zero and a_1 vanishes if the potential is expanded around its minimum.) Therefore, in the solid state limit the phonon feels a harmonic potential. Anharmonic effects only occur due to phonon–phonon interaction. For $N = 1$ the molecular limit is reached and the anharmonicity is seen in the Raman spectrum as a splitting into several vibrational transitions.

In the same way the derivatives of the dielectric function (Equ. 18) can be expressed by the ab-initio results (Equ. 25). For the one–phonon contribution we obtain:

$$\left[\varepsilon_{\mu \rightarrow \nu}^{\alpha\beta} \right]_{\omega_s}^{(1)2} = \left\{ \frac{b_1}{\sqrt{N}f_{\omega_0}} \langle \nu | \hat{Q}_0 | \mu \rangle + \frac{b_2}{Nf_{\omega_0}} \langle \nu | \hat{Q}_0^2 | \mu \rangle + \dots \right\}^2 \quad (27)$$

For very large N only the first term in the brackets can contribute to the scattering efficiency (Equ. 19). No overtones can occur for the one–phonon process. In that case, at zero temperature, and using the vibrational matrix elements of a harmonic oscillator the already known result for the absolute Raman cross section is obtained⁶. The higher–order phonon processes can be estimated by taking only one phononic branch and neglecting any dispersion effects. Then the multi–phonon processes can be obtained from Equ. 18 without any \vec{k} –dependence:

$$\begin{aligned} \left[\varepsilon_{\mu \rightarrow \nu}^{\alpha\beta} \right]_{\omega_s}^{(2)2} &\sim (N-1) \left\{ \frac{b_2}{Nf_{\omega_0}} \langle \nu | \hat{Q}_0^2 | \mu \rangle + \frac{b_4}{N^2 f_{\omega_0}^2} \langle \nu | \hat{Q}_0^4 | \mu \rangle + \dots \right\}^2 \\ \left[\varepsilon_{\mu \rightarrow \nu}^{\alpha\beta} \right]_{\omega_s}^{(3)2} &\sim (N^2-1) \left\{ \frac{b_3}{(Nf_{\omega_0})^{3/2}} \langle \nu | \hat{Q}_0^3 | \mu \rangle + \dots \right\}^2 \\ \dots &\text{etc.} \end{aligned} \quad (28)$$

For large N only the first terms contribute to the multi–phonon spectrum whereas in the limit $N = 1$ no multi–phonon contributions exist and the overtones are caused by a single vibration.

In a similar way the interaction of one ($\vec{k} = 0$) phonon with all the others can be estimated in order to achieve a potential better than that of Equ. 24. Again we neglect dispersion effects and consider only one phononic branch. The contribution of the $N - 1$ remaining phonons to the quantity $u_{\omega_{\vec{k}}}$ characterizing the specific vibration of interest can be estimated by thermal averaged expectation values of the n –th power⁷:

$$\overline{u^n} = \frac{\sum_{\lambda} e^{-E_{\lambda}/k_B T} \langle \lambda | u^n | \lambda \rangle}{\sum_{\lambda} e^{-E_{\lambda}/k_B T}} \left(1 - \left(\frac{1}{\sqrt{N}} \right)^n \right) \quad (29)$$

The factor containing \sqrt{N} is due to the fact that we have only to sum over $N - 1$ phonons in the branch. Inserting this contribution into Equ. 24 the original potential is changed and we obtain new (temperature dependent) coefficients:

$$\begin{aligned}
A_0 &= a_0 + a_1\overline{u^1} + a_2\overline{u^2} + a_3\overline{u^3} + a_4\overline{u^4} + \dots \\
A_1 &= a_1 + 2a_2\overline{u^1} + 3a_3\overline{u^2} + 4a_4\overline{u^3} + \dots \\
A_2 &= a_2 + 3a_3\overline{u^1} + 6a_4\overline{u^2} + \dots \\
A_3 &= a_3 + 4a_4\overline{u^1} + \dots \\
A_4 &= a_4 + \dots \\
\dots &\quad \text{etc.}
\end{aligned} \tag{30}$$

For symmetric potentials only even n contribute and cause no shift of the potential but a change of frequency. In the harmonic case old and new potential are the same. For a local mode or a molecule ($N = 1$) all $\overline{u^n}$ vanish and the potential seen by the vibration is not modified. Odd n contributions cause a shift of the minimum. If the modified potential parameters are used in Equ. 26 in order to calculate the vibrational matrix elements (Eqs. 27 and 28) the calculated Raman spectrum is obtained including temperature dependent anharmonic coupling and size effects (variations in N). This formalism has been applied to the apical oxygen vibration in $\text{YBa}_2\text{Cu}_3\text{O}_7$ described by Ambrosch–Draxl et al.⁴ in this volume.

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