On the Raman shift in nanosized crystals

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Abstract. An analytical form of the Raman shift dependence on size of nanocrystals is presented. Based on the hard confinement model, it works in those cases where the average phonon curve shows a quadratic dependence on the phonon quasi-momentum in the range of interest.

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Raman spectroscopy is an important tool in gathering information about molecular and crystal vibrational properties. Raman spectra can show significant changes when sizes of investigated crystals go down to the nanometer scale. Strain, stress and non-stoichiometry can be invoked to explain these changes \cite{1,2}. However, many published works have shown that in most cases the main cause of spectra changes is to be ascribed to the phonon confinement (PC) effect \cite{3−9}. Actually, the confinement of the $q_0 = 0$ phonon wave function in nanometric-sized crystals makes accessible to Raman investigation a significant portion of the Brillouin Zone (BZ), whose extension increases as the crystal size decreases \cite{3−5}. Besides some specific cases \cite{5,10,11}, a direct relation, even when approximated, which explicitly shows the connection between Raman shift and crystal size, depending on suitable model parameters, is still not available. In this letter we present a detailed numerical analysis of the hard confinement model (HC) which yields an unexpectedly simple analytical form capable of closely reproducing the model predictions. It uses the quadratic approximation of the crystal phonon curve $\omega(q)$ which, in several practical cases, holds down to a few nanometers of crystal sizes.

Formally, the PC effect can be explained by considering the modulation of the phonon wave function in the infinite crystal with a suitable "weighting" function \cite{4}. On expansion by Fourier integrals, we can calculate the first order Raman spectrum of a nano-sized crystal as

\[
I(\omega) \propto |n(\omega) + 1| \int_{BZ} \frac{|C(q)|^2}{|\omega - \omega(q)|^2 + (\Gamma_0/2)^2} dq
\]

where $C(q)$ stand for Fourier coefficients of the $q_0 = 0$ phonon wave function, $\omega(q)$ for the phonon dispersion curve, $\Gamma_0$ for the intrinsic Raman band linewidth.
and \( n(\omega) + 1 \) for the Bose-Einstein factor [4]; the latter being usually disregarded for lineshape characterization or nanoparticle sizing. Some simplifications are required in order to handle eq (1). A drastic but commonly accepted assumption considers an isotropic dispersion in a spherical BZ [4]. In this case, the function \( \omega(q) \) represents an average dispersion curve [6]. As concerns phonon confinement, the HC model assumes a gaussian weighting function for spherical nanocrystals. Accordingly, by disregarding unessential factors, eq (1) can be rewritten as [6, 8, 15]

\[
I(\omega) = \frac{\pi}{a} \int_0^{\pi/a} \frac{\exp(-q^2L^2/16\pi^2)}{[\omega - \omega(q)]^2 + (\Gamma_0/2)^2} dq
\]

(2)

where \( L \) stands for the particle size and \( a \) for the lattice parameter. The latter equation marks the start line of the present work.

If the quadratic approximation holds the phonon curve \( \omega(q) \) can be represented as

\[
\omega(q) = \omega_0 + Aq^2 a^2/2
\]

(3)

where \( A \) stands for a suitable curve parameter. Equation (3) provides an univocal correspondence between peak frequency \( \tilde{\omega} \) and an effective quasi-momentum \( \tilde{q} \) which allows for \( \tilde{\omega} = \omega(\tilde{q}) \). Thus, we should search for an expression of \( \tilde{\omega} \) by investigating the proper definition of \( \tilde{q} \).

For convenience, let us define the function

\[
G(q, L) = q^2 \exp(-q^2L^2/16\pi^2)
\]

(4)

so that,

\[
I(\omega) = \frac{\pi}{a} G(q, L) / \left\{ [\tilde{\omega} - \omega(q)]^2 + (\Gamma_0/2)^2 \right\} dq.
\]

By taking into account that at the maximum of \( I(\omega) \) the condition \( dI(\omega)/d\omega |_{\omega=\tilde{\omega}} = 0 \) holds, we obtain the exact equation

\[
\int_0^{\pi/a} G(q, L) \frac{\tilde{\omega} - \omega(q)}{[\tilde{\omega} - \omega(q)]^2 + (\Gamma_0/2)^2} dq = 0
\]

(5)

Of course, in the framework of the HC model the latter equation is general, that is, not related to a special law for \( \omega(q) \). Thus, for a given \( \Gamma_0 \) and \( \omega(q) \), we can define the distribution-like function

\[
F_{\tilde{\omega}}(q, L) = \frac{G(q, L)}{\left\{ [\tilde{\omega} - \omega(q)]^2 + (\Gamma_0/2)^2 \right\}^{3/2}} / \int_0^{\pi/a} \frac{G(q, L)}{\left\{ [\tilde{\omega} - \omega(q)]^2 + (\Gamma_0/2)^2 \right\}^{3/2}} dq
\]

(6)

so that

\[
\tilde{\omega} = \int_0^{\pi/a} F_{\tilde{\omega}}(q, L)\omega(q) dq
\]

(7)
Now, by inserting form (3) into eq. (7) we can make explicit the meaning of the effective quasi-momentum $\tilde{q}$, that is,

$$\tilde{\omega} = \omega_0 + \frac{A}{2} a^2 \int_0^{\pi/a} \omega(q, L) q^2 dq = \omega_0 + \frac{A}{2} a^2 \tilde{q}^2 \quad (8)$$

The analytical resolution of eq. (5) is quite concealed and its reduction to a differential equation, even if simplified, is not helpful for the purpose. However, for the sake of discussion, it is worth while to handle eq. (5) in a more explicit form. By taking into account that $G(\pi/a, L) \approx 0 \ (L \gg a)$ and after integrations by parts, derivations with respect to $L$ and by disregarding small terms we obtain

$$\Theta(L) = \frac{\Lambda(L)}{9 \left[ 1 - \Theta(L) \right]^2 + \Lambda(L)} \left[ 2 + L \frac{d\Theta(L)}{dL} \right] \quad (9)$$

where

$$\Theta(L) = 1 - \frac{L^2 \tilde{q}^2}{24 \pi^2} \quad (10)$$

and

$$\Lambda(L) = \int_0^{\pi/a} F_{\omega}(\xi, L) \frac{(1 - \xi^2) / \xi^2}{(1 - \xi^2)^2 + (1/\tilde{q}a)^4} d\xi \quad (11)$$

with $x = (|A|/\Gamma_0)^{1/2}$. Due to the gaussian factor present in $F_{\omega}(\xi, L)$, if $L$ is sufficiently large with respect to $a$, the upper integration limit can be considered as infinite so that $\Lambda$ could be conveniently presented as a function on $\eta = L/xa$ rather than on $L$. Thus, to avoid confusion, further we use special symbols $\Theta_S(\eta) = \Theta(L)$ and $\Lambda_S(\eta) = \Lambda(L)$ even when small size are considered.

It is evident from eq. (11) that as $L$ increases $\Lambda_S(\eta)$ decreases because $\tilde{q} \to 0$. Thus, for large $L$ the effective quasi-momentum decreases as $\tilde{q}^2 \approx 24 \pi^2 / L^2$ and $\Lambda_S(\eta)$, as well as $\Theta_S(\eta)$, decreases as $\sim 1/\eta^4$. In the range of small sizes, eq. (11) cannot be used. However, from eq. (11) we expect that for vanishing crystal sizes $\Theta_S(\eta) \to 1$ because of $\tilde{q} \to \pi/a$. In the limiting case of $\tilde{q} \to \pi/a$ we expect $\Theta_S(\eta) \sim \exp(-x^2 \eta^2/24)$. A more detailed description of $\Theta_S(\eta)$ is obtained from the numerical calculation of $\tilde{q}$. Results are shown in the inset of Fig.1 as obtained for different $x$ values. For comparison, segments of parabola approaching the curves $-\ln [\Theta_S(\eta)]$ are shown as well. Precisely, parabola have equations $f(\eta) = mx^2 \eta^2 / 24$ where $m = 0.65$, $m = 0.8$, $m = 1$ and $m = 1$ for $x = 0.5$, $x = 1$, $x = 2$ and $x = 3$, respectively.

Usually $A \gtrsim \Gamma_0$ so that our interest will be focused on the $x \gtrsim 1$ curves. For $\eta > 7$ the latter curves are independent of $x$ and quickly approach the straight line $g(\eta) = \eta/12$, maintaining this trend up to $\eta \approx 60$ where $\Theta_S(\eta) \ll 1$ (Fig.1). On account of eq. (10), we should not be concerned about the deviation.
of $-\ln [\Theta_S(\eta)]$ from the linear law since for $\eta \gtrsim 60$ we have $\tilde{q}^2 \approx 24\pi^2/L^2$. Thus we can be confident of the approximation

$$\tilde{q}_{ap}^2 = \frac{24\pi^2}{L^2} [1 - \exp(-L/12ax)]$$  (12)

and, consequently,

$$\omega_{ap}(\tilde{q}) = \omega_0 + 12\pi^2 Aa^2 \frac{L^2}{L^2} [1 - \exp(-L/12ax)]$$  (13)

in the size range $L \gtrsim 10xa$ (fig.1). Of course, when using eq. (13) in practical cases, we should make sure that the quadratic approximation holds down to the size dealt with.

Now, as an example, let us consider the case of Raman shift in titanate $(TiO_2)$ nanocrystals for which was proposed the average phonon curve [12, 13]

$$\omega(q) = \omega_0 + A [1 - \cos(qa)]$$  (14)

where $\omega_0 = 144$ cm$^{-1}$, $A = 20$ cm$^{-1}$, and $a = 0.376$ nm, the linewidth being $\Gamma_0 = 7$ cm$^{-1}$ so that $x = 1.7$. Fig. 2 shows the deviations of Raman shifts from $\omega_0$ as calculated from eq. (2) with $\omega(q)$ given in eq. (14) (circles), as calculated from eq. (8) (triangles), and as calculated from eq. (13) (dashed curve). As expected from Fig. 1, in the range of small sizes, the latter equations underestimate the deviations of shift. However, departure from the exact curve remains relatively small down to 5 nm where the PC model is believed to become unreliable [6, 12, 13].

A further example is given by the case of silicon nanocrystals whose phonon curve, established by neutron scattering measurements [14], is

$$\omega(q) = \left[B_1 + B_2 \cos(qa/4)\right]^{1/2}$$

with $a = 0.5483$ nm, $B_1 = 1.714 \times 10^5$ cm$^{-2}$, $B_2 = 10^5$ cm$^{-2}$, corresponding to $\omega_0 = 520.5$ cm$^{-1}$ and, in the quadratic approximation, $A = -6$ cm$^{-1}$; the linewidth is $\Gamma_0 = 3.6$ cm$^{-1}$ so that $x = 1.3$. In this case deviations have a reversed sign. Departures from the exact curve have roughly the same relative values found in the previous case. It can be noted that because of the factor $1/4$ in the cosine argument, the quadratic approximation appears to hold in the whole range considered.

As a final consideration we note from Fig. 1 that one could improve the approximation of curve (13) (cases $x \gtrsim 1$) by introducing a suitable factor to $\Theta_S(\eta)$. In this connection, we found that $-\ln [\Theta_S(\eta)] = 0.3\eta \exp(-\eta/2) + \eta/12$ improves the agreement down to $\eta \sim 6$. However, in our opinion, this correction does not recompense the loss of simplicity in eq. (13).

In conclusion, we have shown that in the framework of the PC effect as described by the hard confinement model, the Raman shift in nanocrystals can be calculated, with good approximation, by means of a simple analytical form in the size range where the quadratic approximation of the average phonon curve
holds. The goal is that the dependence of shifts on model parameters as well as on particle sizes is immediately recognizable.

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Captions of Figures

Fig. 1 Negative logarithm of the function Θ_S(η)(eq. 10). Inset, dependence of \( -\ln[\Theta_S(\eta)] \) on x for small η: a, x=0.5; b, x=1; c, x=2; d, x=3. Dashed curves represent parabola with equations \( f(\eta) = mx^2\eta^2 \): a, m=0.6; b, m=0.8; c, m=1; d, m=1.

Fig. 2. Deviations of Raman shifts in nanocrystals from the Raman shift in the infinite crystal. Curves are referred to the source equations. The upper curves have been calculated for the Titanate and the lower curves for the Silicon.
Raman shift deviation (cm\(^{-1}\)) vs. L (nm)

- ▼ — Eq. 2
- □ — Eq. 8
- --- — Eq. 13