Resonant hyper-Raman scattering in spherical quantum dots

E. Menéndez-Proupin and C. Trallero-Giner
Departamento de Física Teórica, Universidad de La Habana, Vedado
10400, La Habana, Cuba

A. García-Cristobal
Departamento de Física Aplicada, Universidad de Valencia
E-46100 Burjassot, Spain

A theoretical model of resonant hyper-Raman scattering by an ensemble of spherical semiconductor quantum dots has been developed. The electronic intermediate states are described as Wannier-Mott excitons in the framework of the envelope function approximation. The optical polar vibrational modes of the nanocrystallites (vibrons) and their interaction with the electronic system are analyzed with the help of a continuum model satisfying both the mechanical and electrostatic matching conditions at the interface. An explicit expression for the hyper-Raman scattering efficiency is derived, which is valid for incident two-photon energy close to the exciton resonances. The dipole selection rules for optical transitions and Fröhlich-like exciton-lattice interaction are derived: It is shown that only exciton states with total angular momentum \( L = 0, 1 \) and vibrational modes with angular momentum \( l_p = 1 \) contribute to the hyper-Raman scattering process. The associated exciton energies, wavefunctions, and vibron frequencies have been obtained for spherical CdSe zincblende-type nanocrystals, and the corresponding hyper-Raman scattering spectrum and resonance profile are calculated. Their dependence on the dot radius and the influence of the size distribution on them are also discussed.

63.20.Dj; 68.65.+9; 63.20.-e

I. INTRODUCTION

The research on semiconductor quantum dots (QD’s) has undergone a dramatic increase in recent years, stimulated by their foreseen applications in optics and electronics technology and also due to their nonlinear optical properties. Quantum dot systems based on III-V materials as well as nanocrystallites of II-VI compounds embedded in glass have been thoroughly investigated (for a review see Ref. [2]). Among the scattering mechanisms present in polar semiconductors, the optical phonon emission is known to play a dominant role in QD’s, which can be experimentally investigated by employing a number of methods, such as infrared absorption and Raman scattering. The successful interpretation of light scattering by optical phonons relies upon a good knowledge of the normal vibrational modes. In recent years a phenomenological continuum theory of optical phonons in nanostructures has been elaborated [10, 11], which is in good agreement with ab initio calculations and allows to explain the resonant Raman scattering intensities of phonon modes induced by interface roughness in quantum wells. The theory has also been generalized to deal with quantum wires and quantum dots, and used to study resonant Raman scattering in these systems. In particular, the formalism is applicable to II-VI semiconductor nanocrystallites embedded in glass since they can have dimensions as small as 13 Å, in which case the mechanical confinement of optical vibrational modes has strong effects (in a QD the concept of phonon as an excitation in a periodic system labeled by a wave vector is lost, and therefore we will use the term vibron to denote the QD vibrational modes). As it has been theoretically demonstrated, optical vibrons in spherical nanocrystallites have a mixed longitudinal-transverse character and can exhibit different symmetries. Raman scattering provides a useful tool to investigate experimentally these vibrons, but only spherically symmetric modes are accessible to this technique. In the search of complementary experimental techniques which can overcome this limitation, hyper-Raman (HR) spectroscopy appears to be a suitable candidate. Recently, HR spectroscopy has been used to study the optical vibrational modes of CdS and CuBr QD’s. In this paper we present a theoretical model which allows to study hyper-Raman scattering (HRS) by optical vibrons under resonance conditions, and illustrate it by performing numerical calculations of the scattered intensities in CdSe nanocrystallites. As far as the exciton-lattice interaction is concerned only the Fröhlich coupling is considered here, though it is admitted that the deformation potential interaction might be of importance for photon energies far from the excitonic resonances. The selection rules for the scattering process are worked out and it is shown that in fact HRS can be used to probe optical vibrations with non-spherical symmetry.

The paper is organized as follows. The main concepts underlying the hyper-Raman scattering and the description of the nanocrystal vibrational modes and excitons are outlined in Sec. II. Section III contains the theoret-
ictical expressions for the matrix elements and HRS efficiency, which are used to analyze the selection rules of the scattering process. The calculation of the exciton and vibrational spectra of CdSe nanocrystallites are presented in Sec. IV and the numerical results obtained for the HRS efficiency are reported and discussed in Sec. V. Section VI is devoted to the main conclusions of the work and final comments.

II. THEORY

A. Hyper-Raman efficiency

Hyper-Raman scattering is a nonlinear process which consists of the absorption of two photons of frequency \( \omega_1 \), wave vector \( \mathbf{k}_1 \), and polarization \( \mathbf{e}_1 \) (i = 1, 2), and the emission of one photon (\( \omega_s, \mathbf{k}_s, \mathbf{e}_s \)) with the simultaneous excitation of a number of vibrational modes. \(^\text{[21]}\)

Due to its nonlinear nature, it is convenient to express the HR yield by the normalized (intensity-independent) scattering cross section \(^\text{[22]}\)

\[
\frac{1}{I_i} \frac{d^2 \sigma^{ij}}{d\omega_s d\Omega_s} = \frac{1}{I_i I_j} \frac{d^2 \mathcal{P}_{ij}}{d\omega_s d\Omega_s} ,
\]

(1)

where \( I_i \) and \( I_j \) being the excitation intensities and \( d^2 \mathcal{P}_{ij} \) the scattered power per unit of solid angle \( \Omega_s \) and unit frequency. The scattered power can be related to the probability per unit time \( W(\omega_i, \omega_j, \omega_s; R) \) of a single scattering event in a QD of radius \( R \), so that we can express the normalized differential cross section as \(^\text{[22]}\)

\[
\frac{1}{I_i} \frac{d^2 \sigma^{ij}}{d\omega_s d\Omega_s} = \frac{V^3}{(2\pi)^3} \frac{\omega^3}{\omega_i \omega_j \hbar \omega_s} V(\omega_i, \omega_j, \omega_s; R) ,
\]

(2)

where \( V \) is the normalization volume, \( \eta_i \) (i = 1, 2) and \( \eta_s \) are the nanocrystal refraction indices at \( \omega_i \) and \( \omega_s \), respectively, and \( c \) is the velocity of light in vacuum. According to the Fermi’s Golden Rule, \( W \) can be written as

\[
W(\omega_1, \omega_j, \omega_s; R) = \frac{2\pi}{\hbar^2} \sum_p |M_p(\omega_i, \omega_j, \omega_s; R)|^2 \delta(\omega_i + \omega_j - \omega_p - \omega_s) ,
\]

(3)

where \( M_p \) is the scattering amplitude. Each scattering event is accompanied by the emission of a vibron of frequency \( \omega_p \), and the total scattering probability is obtained after summing over all possible vibron states p. Only vibron emission (Stokes) processes will be considered in this work.

The delta function in (3) can be eventually replaced by a Lorentzian,

\[
\delta(\omega_i + \omega_j - \omega_p - \omega_s) \rightarrow \frac{\hbar}{\pi} \frac{\Gamma_p}{(\hbar \omega_i + \hbar \omega_j - \hbar \omega_p - \hbar \omega_s)^2 + \Gamma_p^2} ,
\]

(4)

in order to take into account the effect of the vibron lifetime \( \tau_p = \hbar / \Gamma_p \) on the line broadening of the HR spectrum.

The scattering amplitude in (3) can be calculated in fourth-order perturbation theory. Under resonance conditions the important contributions to \( M_p \) are illustrated by the diagrams in Fig. 1. In Fig. 1(a), the exciton created in the state \( |\mu_1\rangle \) after the absorption of a photon \( (\omega_i, \mathbf{k}_i, \mathbf{e}_i) \) is first scattered to the state \( |\mu_2\rangle \) by the absorption of a second photon \( (\omega_j, \mathbf{k}_j, \mathbf{e}_j) \). In the next step, the interaction with the lattice induces an exciton transition from \( |\mu_2\rangle \) to \( |\mu_3\rangle \), accompanied by the creation of a vibron of frequency \( \omega_p \). The exciton finally recombines emitting a photon \( (\omega_s, \mathbf{k}_s, \mathbf{e}_s) \). The amplitude corresponding to this process is

\[
M_p^{(a)} = \sum_{\mu_1, \mu_2, \mu_3} \frac{\langle F | \hat{H}_{E-R}^{(s)} | \mu_3 \rangle \langle \mu_3 | \hat{H}_{E-L}^{(j)} | \mu_2 \rangle \langle \mu_2 | \hat{H}_{E-R}^{(i)} | \mu_1 \rangle \langle \mu_1 | \hat{H}_{E-R}^{(i)} | \rangle}{(\hbar \omega_s - E_{\mu_3} + i\Gamma_{\mu_3})(\hbar \omega_i + \hbar \omega_j - E_{\mu_2} + i\Gamma_{\mu_2})(\hbar \omega_i - E_{\mu_1} + i\Gamma_{\mu_1})} ,
\]

(5)

where \( |I\rangle (|F\rangle) \) is the initial (final) state of the scattering process, \( E_{\mu_1} \) and \( \Gamma_{\mu_1} \) are the energies and lifetime broadenings of the excited electronic states \( |\mu_1\rangle \) in the QD. \( \hat{H}_{E-L} \) and \( \hat{H}_{E-R} \) are the Hamiltonian operators for the interaction of the electronic system with the lattice and radiation field, respectively.

Since the interesting range of \( \hbar \omega_i + \hbar \omega_j \) for resonant HR spectroscopy occurs around the fundamental absorption edge \( E_0 \), the relevant resonances in the matrix element \( \langle F | \rangle \) will occur at energies

\[
\begin{align*}
\hbar \omega_i + \hbar \omega_j &= E_{\mu_2} \quad \text{(incoming resonance)} , \quad (6a) \\
\hbar \omega_s &= E_{\mu_3} \quad \text{(outgoing resonance)} . \quad (6b)
\end{align*}
\]

For the process shown in Fig. 1(b) the scattering amplitude is

\[
M_p^{(b)} = \sum_{\mu_1, \mu_2, \mu_3} \frac{\langle F | \hat{H}_{E-R}^{(s)} | \mu_3 \rangle \langle \mu_3 | \hat{H}_{E-R}^{(i)} | \mu_2 \rangle \langle \mu_2 | \hat{H}_{E-L}^{(j)} | \mu_1 \rangle \langle \mu_1 | \hat{H}_{E-R}^{(i)} | \rangle}{(\hbar \omega_s - E_{\mu_3} + i\Gamma_{\mu_3})(\hbar \omega_i - \hbar \omega_p - E_{\mu_2} + i\Gamma_{\mu_2})(\hbar \omega_i - E_{\mu_1} + i\Gamma_{\mu_1})} .
\]

(7)
In Eqs. (3) and (4) it is implicitly understood that the sum over non-topologically equivalent diagrams (i.e., j) must be taken into account. The examination of the energy denominators in Eq. (3) clearly indicates that $|M_p^{(b)}| \ll |M_p^{(a)}|$ in the resonance region $h\omega_i + h\omega_j \sim E_0$. Therefore the contribution from $M_p^{(b)}$ has been dropped out from our theoretical model.

Finally, it must be noted that in real samples the nanocrystallites present a distribution over size and shape. We intend to study here HRS by an ensemble of spherical QD’s characterized by a distribution over radii $F(R)$. The corresponding average (intensity-independent) HRS efficiency \[^{28}\] is given by

$$\left\langle \frac{d^2S_{HR}}{d\omega_s d\Omega_s} \right\rangle = \frac{1}{\langle V_D \rangle} \int \frac{1}{l_s} \frac{d^2\sigma^{ij}}{d\omega_{ij} d\Omega_s} F(R) dR \ , \ (8)$$

where $\langle V_D \rangle$ is the average quantum dot volume.

B. Exciton states

The intermediate electronic virtual states appearing in the HR process (see Eq. (8)) are taken to be size-confined Wannier-Mott excitons, treated in the framework of the envelope function approximation (EFA). The details of this approach can be found in Ref. \[^{16}\], where it is employed for the study of resonant Raman scattering in QD’s. We summarize here, for notation purposes, the main expressions of the exciton model. In the absence of electron-hole interaction, the wave function of an uncorrelated electron-hole pair (EHP) in a spherical QD can be written as

$$\Phi_{\alpha,L,M}(r_e, r_h) = \sum_{m_e, m_h} (l_e l_h m_e m_h | L M) \phi_{n_e, l_e, m_e}(r_e) \phi_{n_h, l_h, m_h}(r_h) \ , \ (9)$$

where $\alpha$ is an abbreviated notation for $\alpha \equiv (n_e, l_e, n_h, l_h)$. The single-particle (electron or hole) wave functions are given by

$$\phi_{n,l,m}(r) = R_{n,l}(r) Y_{l,m}(\Omega) \ . \ (10)$$

The exciton-vibron interaction Hamiltonian operator can be written as

$$\hat{H}_{E-L} = e \hat{\varphi}_F(r_e) - e \hat{\varphi}_F(r_h) \ , \ (12)$$

where $-e$ ($e > 0$) is the electron charge and

$$e \hat{\varphi}_F(r) = \frac{C_F}{\sqrt{R}} \sum_{n_p,l_p,m_p} \sqrt{\frac{\omega_L}{\omega_{n_p,l_p}}} \Phi_{n_p,l_p}(r) \times \left( Y_{l_p,m_p}(\Omega) \hat{b}_{n_p,l_p,m_p} + H.c. \right) \ . \ (13)$$

Here $\hat{b}_{n_p,l_p,m_p}$ is the vibron annihilation operator and $H.c.$ means Hermitian conjugate. The explicit form of the radial function $\Phi_{n_p,l_p}(r)$ can be found in Refs. \[^{14}\] and \[^{15}\].
Since $\omega_{n\nu,lp} \sim \omega_L$ ($\omega_L$ is the bulk LO-phonon frequency at the $\Gamma$-point), we will omit hereafter the factor $\sqrt{\omega_L/\omega_{n\nu,lp}}$ in (13). The Fröhlich constant $C_F$ is given by

$$C_F = \frac{2\pi e^2 \hbar \omega_L}{\epsilon_a} \left( \frac{1}{\epsilon_{a\infty}} - \frac{1}{\epsilon_{a0}} \right), \quad (14)$$

where $\epsilon_a$ is the phonon dielectric constant of the crystallite material.

### III. MATRIX ELEMENTS AND SELECTION RULES

In this section we analyze in detail the matrix elements appearing in Eq. (3), and derive from them the selection rules for the exciton and vibron states which participate in the HR process.

The matrix elements $\langle \mu_1 | \hat{H}_{E-R}^{(i)} | I \rangle$ and $\langle F | \hat{H}_{E-R}^{(s)} | \mu_3 \rangle$ for direct allowed optical transitions between valence ($v$) and conduction ($c$) bands are given by

$$\langle \mu_1 | \hat{H}_{E-R}^{(i)} | I \rangle = e \frac{1}{m_0} \sqrt{\frac{2\pi \hbar}{\omega_{n\nu} j^2}} (\mathbf{e}_v \cdot \mathbf{p}_{cv}) f_{\mu_1}, \quad (15)$$

where $\mathbf{p}_{cv}$ is the interband momentum matrix element between valence and conduction Bloch functions at $k = 0$, and $m_0$ is the free-electron mass. A similar expression can be obtained for $\langle \mu_3 | \hat{H}_{E-R}^{(s)} | F \rangle$. The exciton overlap integral $f_\mu$ is given by

$$f_\mu \equiv f_{N,L,M,P} = \int \Psi_{N,L,M,P}^\dagger (\mathbf{r}, \mathbf{r}) d^3r = \delta_{L,0} \delta_{M,0} \times \delta_{P_1} \sum_{n_e, n_h} \sum_l (-1)^l \sqrt{2l + 1} C_{N_0,0,0,1(n_e, n_h, l, l)} \int_0^\infty R_{n_e,l}(r) R_{n_h,l}(r) r^2 dr. \quad (16)$$

Hence, the annihilation of the first incoming photon with frequency $\omega_1$ creates an exciton in the state with zero angular momentum and even parity,

$$\mu_1 \equiv (N_1, L_1 = 0, M_1 = 0, P_1 = 1),$$

and analogously, the scattered photon of frequency $\omega_s$ is emitted upon the recombinination of an exciton in the state

$$\mu_3 \equiv (N_3, L_3 = 0, M_3 = 0, P_3 = 1).$$

Both exciton states have $L = 0$ and $P = 1$ because the interband transitions induced by the radiation field require the electron and hole to have equal orbital angular momentum quantum numbers, $l_e = l_h$.

A different situation is found when considering the scattering between exciton states induced by the second incoming photon (matrix element $\langle \mu_2 | \hat{H}_{E-R}^{(j)} | \mu_1 \rangle$ in Eq. (11)). Two possibilities arise in this case [27]: On the one hand there may be transitions accompanied by scattering of the electron (or hole) between QD levels corresponding to different bands (interband excitonic transitions), and by the other hand there are also transitions in which the electron and hole remain in the same band, and only the exciton envelope function is affected by the interaction with the radiation field (intraband excitonic transitions). In III-V and II-VI compounds, and for $\hbar \omega_1 + \hbar \omega_j$ around the fundamental absorption edge, the interband excitonic transitions are due to remote bands which are far enough in energy, thus giving a negligible contribution to the scattering amplitude $M_p$. Therefore we consider only intraband excitonic transitions, whose matrix element can be written, in the dipole approximation, as

$$\langle \mu_2 | \hat{H}_{E-R}^{(j)} | \mu_1 \rangle = \int \Psi_{\nu}^\dagger (\mathbf{r}_e, \mathbf{r}_h) \left( \hat{H}_{\nu-R}^{(j)} - \hat{H}_{\nu-R}^{(j)} \right) \Psi_{\mu_1} (\mathbf{r}_e, \mathbf{r}_h) d^3r_e d^3r_h,$$

where

$$\hat{H}_{\nu-R}^{(j)} = \frac{e}{m_\nu} \frac{1}{\sqrt{2\pi \hbar \omega_{n\nu} j^2}} (\mathbf{e}_j \cdot \mathbf{p}_\nu) (\nu = e, h),$$

$\mathbf{p}_\nu = -i\hbar \nabla_\nu$ is the linear momentum operator, and $m_e$ ($m_h$) is the electron (hole) effective mass (taken to be positive).

Using the expansion (11) in (17) we get

$$\langle \mu_2 | \hat{H}_{E-R}^{(j)} | \mu_1 \rangle = e \frac{1}{m_\nu} \sqrt{\frac{2\pi \hbar}{\omega_{n\nu} j^2}} \sum_{\alpha, \alpha'} C_{N_2, L_2, M_2, P_2} (\alpha') C_{N_1, L_1, M_1, P_1} (\alpha) \left\langle \alpha', L_2, M_2 \left| \frac{\mathbf{e}_j \cdot \mathbf{p}_{\nu}}{m_e} - \frac{\mathbf{e}_j \cdot \mathbf{p}_{\nu}}{m_h} \right| \alpha, L_1, M_1 \right\rangle. \quad (19)$$

Let us now concentrate on the electron part of the matrix element appearing in (19). By making use of the operator identity $\mathbf{p}_e = (ie_e/\hbar) [\hat{H}_e, \mathbf{r}_e]$, where $\hat{H}_e$ is the single-electron Hamiltonian, it is easy to find that

$$\langle \mu_2 | \hat{H}_{E-R}^{(j)} | \mu_1 \rangle = e \frac{1}{m_\nu} \sqrt{\frac{2\pi \hbar}{\omega_{n\nu} j^2}} \sum_{\alpha, \alpha'} C_{N_2, L_2, M_2, P_2} (\alpha') C_{N_1, L_1, M_1, P_1} (\alpha) \left\langle \alpha', L_2, M_2 \left| \frac{\mathbf{e}_j \cdot \mathbf{p}_e}{m_e} \right| \alpha, L_1, M_1 \right\rangle.$$

Using the expansion (11) in (17) we get

$$\langle \mu_2 | \hat{H}_{E-R}^{(j)} | \mu_1 \rangle = e \frac{1}{m_\nu} \sqrt{\frac{2\pi \hbar}{\omega_{n\nu} j^2}} \sum_{\alpha, \alpha'} C_{N_2, L_2, M_2, P_2} (\alpha') C_{N_1, L_1, M_1, P_1} (\alpha) \left\langle \alpha', L_2, M_2 \left| \frac{\mathbf{e}_j \cdot \mathbf{p}_e}{m_e} \right| \alpha, L_1, M_1 \right\rangle \times \frac{i}{\hbar} (E_{\alpha', \alpha} - E_{\alpha, \alpha'}) \langle n'_e, n'_h, l'_h, l_h | l_e, l_h, L_1, M_1 \rangle.$$

(20)
The matrix element in the previous equation can be greatly simplified by taking advantage of the theory of angular momentum, as it is explicitly shown in the Appendix. Moreover, for \( L_1 = M_1 = 0 \) (\( l_e = l_h \)), Eq. \( \text{(20)} \) reduces to:

\[
\langle n_e, n_h, l' e, l' h | n_e, n_h, l_e, l_e, 0, 0 \rangle = \delta_{n_e, n_h} \delta_{l' e, l e} \delta_{L_2, 1} \delta_{P_2, 1} a_{M_2} \times \frac{i R}{\hbar} \frac{1}{\sqrt{3}} (E_{n' e, l'_ e} - E_{n_e, l_e}) \left[ \sqrt{\frac{l_e + 1}{2l_e + 1}} \delta_{l' e, l e + 1} - \sqrt{\frac{l_e}{2l_e + 1}} \delta_{l' e, l e - 1} \right] G_{n_e, l_e \rightarrow n' e, l'_ e},
\]

(21)

\[
G_{n, l \rightarrow n', l'} = \frac{1}{R} \int_0^\infty R_{n', l'}(r) R_{n, l}(r) r^3 \, dr.
\]

(22)

The final expression for the matrix element \( \text{(13)} \) can be arranged in the form

\[
\langle \mu_2 | \hat{H}_{E-L}^{(j)} | \mu_1 \rangle = i e E_0 R^2 \frac{1}{h R} \sqrt{\frac{2 \pi h}{\omega_j}} \left[ \mathcal{F}^{(e)}_{\mu_1 \rightarrow \mu_2} - \mathcal{F}^{(h)}_{\mu_1 \rightarrow \mu_2} \right],
\]

(23)

where we have introduced the energy \( E_0 = \hbar^2 / 2 m_0 R^2 \) (\( R \) is the average QD radius) to make \( \mathcal{F}^{(e,h)} \) dimensionless. The explicit expression for \( \mathcal{F}^{(e)}_{\mu_1 \rightarrow \mu_2} \) is

\[
\mathcal{F}^{(e)}_{\mu_1 \rightarrow \mu_2} = \frac{1}{R} \left[ \frac{E_{n', l'_ e} - E_{n_e, l_e}}{\sqrt{3 E_0}} \right] \delta_{L_2, 1} \mid L_2, 1 \rangle \langle h, 2 | a_{M_2} \sum_{n, n'} \delta_{L_3, 1} \delta_{n', n} C_{n, l_e}^* (\alpha') C_{\mu_1, (\alpha)} \times \left( \frac{R}{R} \right)^2 \left( \frac{E_{n', l'_ e} - E_{n_e, l_e}}{\sqrt{3 E_0}} \right) \frac{1}{\sqrt{3}} \delta_{l' e, l e + 1} - \sqrt{\frac{l_e}{2l_e + 1}} \delta_{l' e, l e - 1} \right] \langle n_e, l_e \rightarrow n' e, l'_ e \rangle.
\]

(24)

A similar expression holds for \( \mathcal{F}^{(h)}_{\mu_1 \rightarrow \mu_2} \) after the exchange of the subscripts \( e \) and \( h \).

An important consequence to be drawn from \( \text{(24)} \) is that after the absorption of the second incoming photon, the exciton must be in the state:

\[
\mu_2 \equiv (N_2, L_2 = 1, M_2 = 0, \pm 1, P_2 = -1) .
\]

Otherwise stated, two-photon absorption generate excitons in \( L = 1 \) states, in contrast to one-photon transitions for which the final exciton state is necessarily \( L = 0 \). Moreover, the factor \( \delta_{l' e, l e \pm 1} \) in Eq. \( \text{(24)} \) introduces the parity selection rule \( P_1 = 1 \rightarrow P_2 = -1 \), indicating that the intraband transitions are accompanied by a change in the parity of the excitonic state. If the incident light is linearly polarized with \( \mathbf{e}_j \parallel \hat{z} \) then \( a_{M_2} = \delta_{M_2, 0} \) (see the Appendix), whereas for circular polarization \( \mathbf{e}_j \parallel (\hat{x} \pm i \hat{y})/\sqrt{2} \) we have \( a_{M_2} = \delta_{M_2, \pm 1} \) (\( \hat{x}, \hat{y} \) represent some system of orthogonal axes attached to the laboratory frame). Hence, the \( L_2 = 1 \) excitonic states participating in the HRS process have \( M_2 = 0 \) for linearly polarized light and \( M_2 = \pm 1 \) for circularly polarized light.

Now we turn to the matrix element of the exciton-lattice interaction \( \langle \mu_3 | \hat{H}_{E-L} | \mu_2 \rangle \). If we select the vibron creation terms in \( \text{(13)} \) and make use of \( \text{(11)} \), we get the expression

\[
\langle \mu_3 | \hat{H}_{E-L} | \mu_2 \rangle = \frac{C_F}{\sqrt{R}} \sum_{\alpha', \alpha''} C_{N_3, L_3, M_3, P_3, \alpha''}^* C_{N_2, L_2, M_2, P_2, \alpha'} \times \sum_{n, l, m} \left\langle \Phi_{n(p), l} (r_e) Y_{l, m}^* (\Omega_e) - \Phi_{n(p), l} (r_h) Y_{l, m}^* (\Omega_h) \right| \alpha', L_2, M_2 \right\rangle,
\]

(25)

which consists again of separated electron and hole contributions, each of them being a sum of matrix elements of spherical tensors. Therefore the method used previously for the intraband exciton-photon matrix elements (see the Appendix) applies also here. By following that procedure, and considering that \( L_2 = 1, L_3 = M_3 = 0 \), Eq. \( \text{(23)} \) is reduced to

\[
\langle \mu_3 | \hat{H}_{E-L} | \mu_2 \rangle = \frac{C_F}{\sqrt{R}} \left[ \mathcal{H}^{(e)}_{\mu_2 \rightarrow \mu_3} - \mathcal{H}^{(h)}_{\mu_2 \rightarrow \mu_3} \right],
\]

(26)

where
\[ \mathcal{H}_{p_2 \to \mu_3}^{(c)} = \delta_{p_1,1} \delta_{m_p,M_2} \sum_{\alpha',\alpha''} \delta_{\alpha'_n,\alpha''_n} \delta_{\alpha'_m,\alpha''_m} C^{*}_{\alpha''}(\alpha'') C_{\mu_2}(\alpha') \\
\times \frac{1}{\sqrt{4\pi}} \left[ \sqrt{\frac{2\mu'}{\bar{\omega}'_l}} + 1 - \sqrt{\frac{2\mu'}{\bar{\omega}'_l} + 1} \delta_{\alpha'_n,\alpha''_n} \right] \Phi_{n',l' \to \alpha''_n,\alpha''_m}^{n_p,l_p} , \]  
(27)

\[ \Phi_{n',l' \to \alpha''_n,\alpha''_m}^{n_p,l_p} = \int_0^{\infty} R_{n'',l''}(r) R_{n',l'}(r) \Phi_{n_p,l_p}(r) r^2 \, dr . \]  
(28)

An analogous expression to (27) holds for \( \mathcal{H}_{\mu_2 \to \mu_3}^{(h)} \) after the exchange of the subscripts \( e \) and \( h \).

It follows from (27) that the quantum numbers of the emitted vibron are fixed to be \( l_p = 1 \) and \( m_p = M_2 \).

The different states \( m_p \) can be discriminated by selecting adequately the polarization \( \varepsilon_j \) of the exciting light: \( M_2 = m_p = 0 \) if \( \varepsilon_j \parallel \hat{z} \) and \( M_2 = m_p = \pm 1 \) if \( \varepsilon_j \parallel (\hat{x} \pm i\hat{y})/\sqrt{2} \). Thus, the HR selection rules in a spherical QD can be expressed schematically by the following sequence of states.

\[ (L_1 = 0, M_1 = 0) \rightarrow (L_2 = 1, M_2 = 0, \pm 1) \rightarrow (L_3 = 0, M_3 = 0) \]  
(29)

which contrasts with that corresponding to Raman scattering [3][10]

\[ (L_1 = 0, M_1 = 0) \rightarrow (L_2 = 0, M_2 = 0) \]  
(30)

where only \( l_p = 0 \) vibrons can be excited. The comparison between (26) and (29) makes up clear the complementariness of both light scattering techniques to study the vibrational spectra of spherical QD’s. In particular, we have shown that hyper-Raman spectroscopy can be used to investigate the \( l_p = 1 \) vibronic states, not observable in Raman scattering. In addition, the analysis of the corresponding resonance profiles (scattering efficiency vs. \( h\omega_i + \hbar\omega_j \)) can be useful to reveal \( L = 1 \) excitonic states. Of course, the selection rules discussed can be relaxed when going beyond our simplified treatment of the HR process, e.g. including valence band mixing. Nevertheless, for \( R \) smaller than the bulk exciton Bohr radius the separation in energy between the \( hh \) and \( lh \) levels induced by the confinement should lead to a small amount of \( hh-lh \) admixture.

Finally, by inserting Eqs. (15), (23), and (26) into (3), we obtain the following compact expression for the normalized scattering cross section

\[ \frac{1}{L_i} \frac{d^2 \sigma_{ij}}{d \omega_i d\Omega} = \sigma_0 \left( \frac{R}{R} \right)^3 \sum_{n_p} \sum_{\eta_i,\eta_j} \left( \frac{\omega_i}{\omega_j} \right)^2 | \mathcal{M}_{n_p}(\omega_i, \omega_j, \omega_s; R) |^2 \Delta(\omega_s) , \]  
(31)

where \( \mathcal{M}_{n_p} \) is the dimensionless amplitude

\[ \mathcal{M}_{n_p} = E_0^3 \sum_{\mu_1,\mu_2,\mu_3} \int_{\Omega_3} [ \mathcal{H}_{\mu_2 \to \mu_3}^{(c)} - \mathcal{H}_{\mu_2 \to \mu_3}^{(h)} ] - \mathcal{F}_{\mu_3 \to \mu_2}^{(c)} - \mathcal{F}_{\mu_3 \to \mu_2}^{(h)} \]  
(32)

and

\[ \sigma_0 = 2\pi \frac{e^6}{m_0^2 \hbar^2} \frac{\bar{R}^2}{(\hbar \omega_i)^2} | \varepsilon_i \cdot \mathbf{p}_{ex} |^2 | \varepsilon_s \cdot \mathbf{p}_{ex} |^2 \frac{C_F^2}{E_0^2 R^3} . \]  
(33)

The expression (31) is suitable for the calculation of the scattered spectrum as a function of the HR shift, \( \omega_s - \omega_i - \omega_j \). If we are interested in the resonance behavior of the scattered intensity we can obtain the average HRS efficiency by integrating Eq. (8) over \( \omega_s \),

\[ \left\langle \frac{dS_{HR}}{d\Omega} \right\rangle = \left\langle \frac{\sigma_0}{V_D} \right\rangle \sum_{n_p} \int_{\eta_i,\eta_j} \left( \frac{\omega_i + \omega_j - \omega_{n_p}(R)}{\omega_j} \right)^2 \left( \frac{R}{R} \right)^3 | \mathcal{M}_{n_p}(\omega_i, \omega_j, \omega_i + \omega_j - \omega_{n_p}(R); R) |^2 \, F(R) \, dR , \]  
(34)

where \( \left\langle \sigma_0 \right\rangle \) is the average of \( \sigma_0 \) over the QD orientations in the ensemble. For typical values of \( \bar{R} \sim 20 \text{ Å} \) and, \( E_0 \sim 10 \text{ meV} \), and the parameters of Table II a value of \( 10^{-4} \text{ cm}^{-1} \) is estimated for \( \left\langle \sigma_0 \right\rangle / (V_D) \). In the case of an ensemble of QD’s the HRS efficiency is replaced by the average over the QD orientations with the angle \( \arccos(\varepsilon_i \cdot \varepsilon_s) \) fixed.

From now on we focus on the degenerate case, \( \omega_i = \omega_j = \omega_1 \), with \( 2\omega_1 \) in the region around the excitonic transitions, which is the usual situation for resonant HRS experiments.

**IV. EXCITON ENERGIES AND VIBRONS IN CDSE NANOCRYSTALLITES**
where \( j_i \) is the spherical Bessel function and \( x_n^l \) are the roots of \( j_i(x_n^l) = 0 \). The single-particle energies are given by

\[
E_{n,l} = \frac{\hbar^2}{2m_0 R^2} x_n^l \, .
\]

First, we present in Fig. 2(a) the exciton energies, calculated as explained in Sec. I, for a CdSe quantum dot as a function of the radius. The material parameters used as input are shown in Table I. Solid and dashed lines correspond to \( L = 0 \) and \( L = 1 \) excitons, respectively.

According to Ref. [1] we have taken into account the penetration of the wave function in the glass matrix by using an effective radius \( R_{eff} = 3.367 + 0.9078 R \) (in Å), where \( R \) is the nominal QD radius.

Let us focus now the attention on the vibrational modes. Since the active TO-phonon branch of hexagonal CdSe seems to be flat [28], the parameter \( \beta_T \) appearing in the isotropic model for the optical vibrations has been taken as the limit \( \beta_T \to 0^+ \), with a negative bulk dispersion relation \( \omega^2 = \omega_p^2 - \beta_T^2 \omega^2 \). If one attempts to solve the vibron model of Ref. [1] with \( \beta_T = 0 \), it is not possible to fulfill all the matching boundary conditions at the interface. What is expected on physical grounds is that the TO component of the vibron vector displacement, at forbidden frequency for pure TO phonons, is a vanishing or rapidly decaying function. This can be verified in the solution for the vibrational amplitude \( u(r) \) (Eqs. (35) and (36) of Ref. [14]). The TO component of \( u \) vanishes for all \( r < R \) in the limit \( \beta_T \to 0^+ \).

Figure 2(b) illustrates the allowed frequencies for the \( l_p = 1 \) optical vibrons as a function of the QD radius. Below \( \omega_L = 213 \) cm\(^{-1} \) it can be seen the confined LO modes with both longitudinal and transverse components, including a surface mode contribution. We can observe some bending in the dispersion around 185 cm\(^{-1} \), which is identified as the Fröhlich mode.

This mode arises in the framework of dielectric models, which neglect the effect of mechanical boundary conditions and consider flat bands for TO and LO bulk phonons. The Fröhlich frequency \( \omega_F \) is related only to the dielectric constants of the constituent media: \( \omega_F^2 = \omega_p^2 (\epsilon_0 + 2 \epsilon_{\infty}) / (\epsilon_{\infty} + 3 \epsilon_{\infty}) \). A strong electrostatic contribution is expected in the dispersion for vibron frequencies close to \( \omega_F \). In Fig. 3 we depict the electrostatic potential \( \Phi_{n_p,1}(r) \) as a function of \( r \) for QD radii \( R = 11.5 \) Å, 16.2 Å, and 21 Å. At these radii, \( \omega_{n_p,1} \) equals \( \omega_F \) for \( n_p = 2, 3, \) and 4. It can be seen that the electrostatic potential \( \Phi_{n_p,1} \) shows an enhancement close to the interface whenever \( \omega_{n_p,1} \) coincides with \( \omega_F \).

V. SCATTERING INTENSITIES

In this Section the results obtained with Eqs. (31)-(34) for the HRS spectrum and resonance profile in CdSe QD’s are shown. The incoming (outgoing) resonances will be denoted by the combination of the letter I (O) and the exciton quantum number \( N \) of the corresponding resonant levels. It is important to remind the selection rules already discussed in Sec. I. The relevant incoming resonances take place at \( 2h\omega_L = E_{N,L=1,M,-1} \) whereas the outgoing ones appear at \( h\omega_m = E_{N,L=0,0,1} \).

In the next discussion we first analyze the hyper-Raman process for the case in which all the nanocrystals in the sample have the same radius \( R \). Typical HRS spectra are shown in Fig. 4 for different QD radii. The incident photon energy is such that \( h\omega_m = 2h\omega_L - h\omega_1 \) is in resonance with the \( N = 1, L = 0 \) excitonic level. We have included in the calculation the lowest 11 QD excitonic levels (\( N = 1 \) to 11, for each value \( L = 0, 1 \)). A lifetime broadening \( \Gamma_\mu = 5 \) meV was assumed for all excitonic transitions. The spectra are broadened to have a full width at half maximum (FWHM) \( 2\Gamma_{n_p} = 4 \) cm\(^{-1} \). It is systematically found that the main peak of the spectrum corresponds to the creation of the \( l_p = 1, n_p = 1 \) vibron, with a small contribution coming from the \( n_p = 2, 3, 4 \) vibrons. This is related to the fact that the matrix element \( \mathcal{H}_{n_1 n_2 \to n_3} \) drops off rapidly as \( n_p \) increases. It must be noted that in the spectra 4(a) and 4(b) the \( n_p = 3 \) peak is stronger than the \( n_p = 2, 4 \) ones, while the largest contribution in spectrum 4(c) (aside from the main line) is due to the \( n_p = 4 \) peak. This difference can be explained in terms of the electrostatic effects discussed above: If one looks back to the vibron frequencies as a function of the QD radius in Fig. 2(b), it can be realized that for \( R = 16 \) Å and 18 Å the vibron frequency \( \omega_{3,1} \) is around the Fröhlich frequency \( \omega_F \), and thus the exciton-vibron interaction is dominant for these modes in the corresponding spectra 4(a) and 4(b). For \( R = 21 \) Å, on the other hand, \( \omega_{4,1} \) is approximately equal to \( \omega_F \) and therefore its potential gives an enhanced contribution to the exciton-vibron interaction (see also Fig. 3), which is reflected in the spectrum 4(c).

The HR resonance profile (scattering efficiency vs. \( 2h\omega_{L} \)) for the \( n_p = 1, l_p = 1 \) vibron peak is displayed as a solid line in Fig. 4 for QD radius \( R = 18 \) Å. The most important feature of Fig. 4 is that the O1 (\( L = 0 \)) resonance takes place at lower energy than the I1 (\( L = 1 \)) resonance, which is a natural consequence from the spacing between excitonic levels being much larger than the vibron frequencies. It is worth pointing out that the opposite situation is usually encountered in bulk semiconductors. We have also calculated the HRS intensity taking the Coulomb interaction equal to zero, recovering the free electron-hole model [13] (dashed line), and treating the Coulomb interaction just in first order perturbation theory (dotted line). It is apparent the exciton redshift when the electron-hole interaction is included. Also,
when comparing the absolute values of the scattering intensities for the different approaches we see that the full calculation is extremely well approximated by the perturbative approach and gives only slightly larger values than the free electron-hole model (mainly due to the enhanced oscillator strengths of \( L = 0 \) excitons). Concerning to the HR cross section the free electron-hole model presents identical lineshapes to those displayed in Fig. 2, whenever \( 2\hbar\omega_r \) is rescaled to set the equivalent resonance conditions. Thus, we conclude that the excitonic effects on the HR resonance profile (and also on the HR spectrum) of quantum dots in the strong confinement regime stand mostly to renormalize the resonance energies.

Let us finally discuss the effects of the size dispersion of the crystallites on the HRS spectrum. We have considered an ensemble of QD’s described by a Gaussian distribution function \( F(R) \) centered at the mean radius \( \bar{R} \) and with FWHM equal to 40%. For a given incoming photon energy \( \hbar\omega_l \), Eqs. (6) determine a set of resonance radii \( \{ \bar{R}_r \} \) and their corresponding resonant exciton levels \( \{ E_r \} \) with lifetime broadenings \( \{ \Gamma_r \} \). These are marked by arrows in Fig. (a), at \( 2\hbar\omega_l = 2.771 \) eV. As \( \bar{R} \) departs from \( \bar{R}_r \), the resonance condition ceases to hold rapidly. The range \( \delta R_r \) around the resonance radius \( \bar{R}_r \) which contributes to the integral in Eq. (34) is typically of the order of some tens of Angstrom. In such a small interval, the matrix elements and the vibron frequencies in Eq. (33) can be considered as constants. On these grounds we have employed the following approximation

\[
\int \frac{d^2\sigma(R)}{d\Omega_s d\omega_s} F(R)dR \to \sum_r \frac{d^2\sigma(R_r)}{d\Omega_s d\omega_s} F(R_r)\delta R_r . \tag{37}
\]

An estimation for \( \delta R_r \) can be obtained from

\[
\delta R_r = \frac{\pi \Gamma_r}{\frac{dE_r}{dR} |_{R_r}} . \tag{38}
\]

Note that as the HR spectrum evaluated at the resonance radius \( \bar{R}_r \) is proportional to \( \Gamma_r^{-2} \) and \( \delta R_r \) is proportional to \( \Gamma_r \), the contribution of the \( \bar{R}_r \)-resonant QD’s to the average HR spectrum is proportional to \( 1/\Gamma_r \).

In Fig. (b) we show the averaged HR spectrum of the ensemble of CdSe spherical nanocrystallites with a mean radius of 21 Å, obtained when \( 2\hbar\omega_l = 2.771 \) eV. This two-photon energy determines a set of incoming and outgoing resonances with different exciton levels for QD’s with different radii \( \bar{R}_r \), which are listed in Table (1) (for the emission of the \( n_p = 1, l_p = 1 \) vibron). The contributions of the various \( \bar{R}_r \) are also shown in Fig. (b). The resonances due to other exciton levels either are too weak or are attenuated by the size distribution function. Two important features of the HR spectrum deserve special attention. The first one is the main peak at about 208 cm\(^{-1}\), which is originated by the emission of the \( n_p = 1, l_p = 1 \) vibrons in QD’s with different resonance radii. The most important contribution is that of the outgoing resonance O3 which takes place for \( R = 28.0 \) Å. This resonance appears so strongly because a double resonance condition connecting the levels \( N = 3, L = 0 \) and \( N = 3, L = 1 \) is almost fulfilled (see Fig. (a)). In addition the resonance I3, associated to dots of radius \( R = 27.8 \) Å, is very close in energy to O3. The second important feature is the broad structure between 180 and 190 cm\(^{-1}\). This structure is caused by the emission of interface-like vibrons from all resonant QD’s. Its irregular shape is a direct consequence of the vibron frequency dispersion as a function of QD radius.

Figure (b) shows the variation of the HR lineshapes with small variations of the incoming photon energy for an ensemble of QD’s with a mean radius of 18 Å. When \( 2\hbar\omega_l = 2.771 \) meV increases (decreases) by 100 meV, the radii of resonance get smaller (larger) by about 1 Å (see Fig. (a)). Hence, the principal peak of the spectrum is shifted to high (low) frequencies, as can be seen in the four lower curves of the figure. Nevertheless, an opposite effect appears in the upper spectrum (change from \( 2\hbar\omega_l = 2.771 \) eV to \( 2\hbar\omega_l = 2.971 \) eV): In this special situation the higher resonance radii get closer to the mean radius \( \bar{R} = 18 \) Å and become dominant in the spectrum. This effect is equivalent to an increase of the mean radius. It is important to note that the FWHM of the spectrum at \( 2\hbar\omega_l = 2.771 \) eV is larger than at \( 2\hbar\omega_l = 2.671 \) eV as a result of the competition between the large contributions of the resonance radii.

Finally, the dependence of the HR lineshape on the mean radius for \( 2\hbar\omega_l = 2.771 \) eV is shown in Fig. (b). The main features can be explained with similar arguments as in the previous figures. For \( \bar{R} = 15 \) and 16 Å the lineshapes are practically identical due to the resonance O1 in the dots of radius \( R = 18 \) Å. For \( \bar{R} = 18 \) Å the maximum is slightly shifted to high frequencies reflecting the influence of other resonances associated with larger radii. For \( \bar{R} = 21 \) Å the main peak is not Lorentzian, showing the contribution of several equally-strong resonances. And for \( \bar{R} > 21 \) Å the resonance O3 becomes dominant.

VI. CONCLUSIONS

We have developed a formalism to calculate the normalized hyper-Raman scattering efficiency in spherical semiconductor quantum dots, considering confined Wannier-Mott excitons as the intermediate states. The exciton-lattice interaction is assumed to occur via Fröhlich-type coupling. It has been shown that hyper-Raman spectroscopy can be used to probe the \( l_p = 1 \) vibrational modes. In addition, each particular mode \( (m_p = 0, \pm 1) \) can be selected by properly choosing the polarization of the incident light. With linearly polarized incident light, only \( m_p = 0 \) vibrons contribute to the scattering whereas by employing circularly polarized light the \( m_p = \pm 1 \) modes are active. The details of
the calculations of the polar optical vibrational modes in CdSe QD's have been discussed and the eigenfrequencies and electrostatic potentials of the \( l_p = 1 \) modes have been presented as a function of the nanocrystallite radius. It has been demonstrated that when their frequencies are close to the Fröhlich frequency, they undergo an increase in their electrostatic surface character.

The calculations of the hyper-Raman spectra show that the most prominent peak is due to the emission of \( n_p = 1, l_p = 1 \) vibrons. The other contributions are due to the interface-like \( l_p = 1 \) vibrons. The presence of surface electronic excitations could increase their role in hyper-Raman scattering.

The effect of the electron-hole Coulomb interaction has been found to be of limited importance for the hyper-Raman scattering in the strong confinement limit relevant to the QD's analyzed here. The absolute values of the HRS intensity are slightly enhanced by the Coulomb interaction as compared to the free electron-hole model values. The main excitonic effect seems to be the renormalization of the resonance energies.

The size dispersion of the nanocrystallites is shown to give rise to a complex behavior of the main peak position in the HR spectrum as a function of the laser energy and the details of the distribution over radii. An additional effect is the distribution of the signal due to interface-like vibrons over a broad band of frequencies from 180 to 190 cm\(^{-1}\).

ACKNOWLEDGMENTS

One of us (E. M.-P.) acknowledges J. L. Peña for his hospitality at CINVESTAV-IPN (Merida, Mexico), where part of this work was performed. We are grateful to Carlos Rodríguez-Castellanos for a critical reading of the manuscript.

APPENDIX: REDUCTION OF THE MATRIX ELEMENTS

In this Appendix we show in detail how to calculate matrix elements of the form

\[
\langle n'_e, n'_h, l'_e, l'_h, L', M'|T_{kq}|n_e, n_h, l_e, l_h, L, M \rangle ,
\]

where \( T_{kq} \) is the \( q \)th component of a \( k \)th-order spherical tensor (single-particle) operator \( T_k \), \( |n_e, n_h, l_e, l_h, L, M \rangle \) represents an electron-hole pair state (see Eq. (9)), and \( (L, M) \) are the corresponding total angular momentum quantum numbers.

First of all, we factorize the dependence on \( M' \), \( M \) and \( q \) by applying the Wigner-Eckart theorem:

\[
\begin{align*}
\langle n'_e, n'_h, l'_e, l'_h, L', M'|T_{kq}|n_e, n_h, l_e, l_h, L, M \rangle &= (-1)^{L'-M'} \left( \begin{array}{c} L' & k & L M \\ -M' & q & M \end{array} \right) \sqrt{2L'+1} \\
&\times \langle n'_e, n'_h, l'_e, l'_h, L'||T_k||n_e, n_h, l_e, l_h, L \rangle .
\end{align*}
\]

Finally, by inserting (A3) into (A2) we achieve the complete simplification of the matrix element (A1).

Let us illustrate this procedure taking as example the matrix element in (20). As a previous step we must realize that the operator \( \mathbf{e} \cdot \mathbf{r}_h \) can be expressed in terms of spherical irreducible tensors,

\[
\mathbf{e} \cdot \mathbf{r}_h = \sum_{q=-1}^{1} a_q T_{1q}^{(e)} , \quad T_{1q}^{(e)} = \sqrt{\frac{4\pi}{3}} r_1 Y_{1,q}^{(e)} ,
\]

with the definitions

\[
a_0 = e_z , \quad a_{\pm 1} = \frac{i e_z \mp e_x}{\sqrt{2}} .
\]

Now, by applying Eqs. (A2) and (A3) we obtain

\[
\left( n'_e, n'_h, l'_e, l'_h, L, M \right) \left( \begin{array}{cccc}
L_e & 1 & L_h & 1 \\
-M_e & M_h & 1 & 1 \\
L_e & l'_e & M_h & l'_h \\
L_h & l'_h & M_e & l'_e \\
0 & 0 & 0 & 0
\end{array} \right) \left( \begin{array}{c}
l'_e \\
l'_h \\
l_e \\
l_h \\
r_e \\
r_h
\end{array} \right)
\]

Proceeding in a similar way it can be shown that an expression analogous to (2) (with subscripts \( e \) and \( h \) exchanged everywhere) holds for the matrix element of the hole operator \( \mathbf{e} \cdot \mathbf{r}_h \). To obtain the last expression we have used the following reduced matrix element

\[
\left( n'_e, n'_h, l'_e, l'_h, L, M \right) \left( \begin{array}{cccc}
L_e & 1 & L_h & 1 \\
-M_e & M_h & 1 & 1 \\
L_e & l'_e & M_h & l'_h \\
L_h & l'_h & M_e & l'_e \\
0 & 0 & 0 & 0
\end{array} \right) \left( \begin{array}{c}
r_e \\
r_h \\
r_e \\
r_h \\
r_e \\
r_h
\end{array} \right)
\]

\[
\times \sqrt{2L_e + 1)(2L_h + 1)(2l'_e + 1)(2l'_h + 1) \int R_{n'_e,l'_e}(r) R_{n_e,l_e}(r) r^3 dr
\]

9
\begin{align}
\langle n', l'|T_1|n, l \rangle &= \sqrt{4\pi/3} \left( \int R_{n', l'}(r) R_{n, l}(r) r^3 \, dr \right) \langle l'|Y_1|l \rangle \\
\langle l'|Y_k|l \rangle &= (-1)^l' \sqrt{(2l + 1)(2k + 1)/(4\pi)} \begin{pmatrix} l' & k & l \\ 0 & 0 & 0 \end{pmatrix}. \tag{8}
\end{align}

In this expression it is implicit that only the creation part of \( \hat{\phi}_{F} \) is acting on the ket. Replacing \( L_2 = 1, L_3 = M_3 = 0 \), the Eq. (8) is reduced to Eq. (27) and \( \Phi_{n^p, l'p, m'p}^{n^e, l'p} \rightarrow n', l' \) is defined in Eq. (28).

Moreover, if we particularize (4) to the case \( L_1 = M_1 = 0 \) \((l_e = l_h)\) and evaluate the \( 3j \) and \( 6j \) symbols we get the result shown in Eq. (22).

Applying the same method the following expression is obtained for the matrix elements of the electron-lattice interaction

\begin{align}
\langle n^e_{n^e, l^e} \rightarrow n^e_{l^e} | \hat{\phi}_{F} | n^e_{n^e, l^e} \rangle &= \sum_{n_p, l_p, m_p} \sqrt{(2l_e + 1)(2l_p + 1)(2l_u + 1)/4\pi} \left( -L_2 \right)_{M_2} \left( l_p \right)_{M_3} \left( \frac{L_3}{M_3} \right) \left( \frac{l_e}{l_u} \right)_{M_e} \left( \frac{l_u}{l_e} \right)_{M_u} \Phi_{n^e_{n^e, l^e} \rightarrow n^e_{l^e}}. \tag{9}
\end{align}

[1] C. W. Beenaker and H. van Houten, in Solid State Physics: Semiconductor Heterostructures and Nanostructures, ed. by H. Ehrenreich and D. Thurnbull (Academic Press, San Diego, 1991), Vol. 44.
[2] U. Woggon and S. V. Gaponenko, Phys. Stat. Sol. (b) 189, 285 (1995).
[3] T. D. Krauss, F. W. Wise, and D. B. Tanner, Phys. Rev. Lett. 76, 1376 (1996).
[4] P. T. C. Freire, M. A. Araujo Silva, V. C. S. Reynoso, A. R. Vay, and V. Lemos, Phys. Rev. B 55, 6743 (1997).
[5] G. Scamarcio, M. Lugara, and D. Manno, Phys. Rev. B 45, 13792 (1992).
[6] A. L. Efros, A. I. Ekimov, F. Kozlowsky, V. Petrovskii-Koch, M. Schmidbaur, and S. Shumilov, Solid State Commun. 78, 853 (1991).
[7] A. V. Fedorov, A. V. Baranov, and K. Inoue, Phys. Rev. B 56, 7491 (1997).
[8] M. C. Klein, F. Hache, D. Ricard, and C. Flytzanis, Phys. Rev. B 42, 11123 (1990).
[9] C. Trallero-Giner, A. Debernardi, M. Cardona, E. Menéndez-Proupin, and A. I. Ekimov, Phys. Rev. B 57, 4664 (1998).
[10] C. Trallero-Giner, F. Garcia-Moliner, V. R. Velasco, and M. Cardona, Phys. Rev. B 45, 11944 (1992).
[11] M. P. Chamberlain, M. Cardona, and B. K. Ridley, Phys. Rev. B 48, 14356 (1993).
[12] C. Trallero-Giner, F. Comas, and F. Garcia-Moliner, Phys. Rev. B 50, 1755 (1994).
[13] A. J. Shields, M. Cardona, and K. Eberl, Phy. Rev. Lett. 72, 412 (1994).
[14] E. Roca, C. Trallero-Giner, and M. Cardona, Phys. Rev. B 49, 13704 (1994).
[15] M. P. Chamberlain, C. Trallero-Giner, and M. Cardona, Phys. Rev B 51, 1680 (1995).
FIG. 1. Feynman diagrams which give the main contribution to the resonant hyper-Raman scattering.

FIG. 2. (a) Energy levels of $N = 1, \ldots, 7$ and $L = 0$ (solid lines) and $L = 1$ (dashed lines) excitons in a spherical CdSe nanocrystallite as a function of its radius. Dashed line I indicates the two-photon energy $2\hbar\omega_l = 2.771$ eV and solid line II corresponds to the scattered photon energy $\hbar\omega_s = 2\hbar\omega_l - \hbar\omega_{1,1} = 2.745$ eV. The solid (dashed) arrows indicate the radii of the corresponding outgoing (incoming) resonances. Line III represents a Gaussian distribution over QD radii centered at $\bar{R} = 18$ Å and with FWHM equal to 40% (see text). (b) Frequency of the $l_p = 1$ optical vibrons of a CdSe nanocrystallite as a function of its radius.

FIG. 3. Plot of the electrostatic potentials associated to the first optical vibrons for different crystallite radii. Solid line: $n_p = 1$; dashed line: $n_p = 2$; dotted line: $n_p = 3$; dot-dashed line: $n_p = 4$. The equation $\omega_{n_p, 1}(R) = \omega_F$ with $n_p = 2, 3, \text{and } 4$ is fulfilled for $R = 11.5$ Å, $R = 16.2$ Å, and $R = 21$ Å, respectively. We see that the electrostatic potential $\Phi_{n_p, 1}$ increases at the interface whenever $\omega_{n_p, 1}$ coincides with the Fröhlich frequency $\omega_F$.

FIG. 4. Hyper-Raman spectra of CdSe nanocrystallites embedded in glass for different radii and two photon energies: a) $R = 16$ Å and $2\hbar\omega_l = 2.979$ eV. b) $R = 18$ Å and $2\hbar\omega_l = 2.775$ eV. c) $R = 21$ Å and $2\hbar\omega_l = 2.559$ eV.

FIG. 5. Hyper-Raman intensity calculated for CdSe nanocrystallites with radius $R = 18$ Å. The resonances are denoted by the labels IN or ON, where I (O) means incoming (outgoing) resonance with the exciton level $N$. Three approaches have been used: Solid line: Full matrix diagonalization including exciton effects. Dotted line: first order perturbation theory for the energy. Dashed line: free electron-hole model.

FIG. 6. Hyper-Raman spectrum for $2\hbar\omega_l = 2.771$ eV of an ensemble of CdSe QD’s with mean radius 21 Å and a 40% size dispersion. The contributions of the QD’s with different resonance radii are also shown.

FIG. 7. Hyper-Raman spectra for an ensemble of QD’s with a mean radius 18 Å and a 40% size dispersion for different values of the laser energy. The inset illustrates the dependence of the maximum position and FWHM on the two photon energy $2\hbar\omega_l$. The lines are a guide to the eyes.

FIG. 8. Dependence of the HR lineshape with the mean radius $\bar{R}$ at $2\hbar\omega_l = 2.771$ eV. The size dispersion is 40% of the mean radius in all the spectra.
TABLE I. Values of the material parameters used for the numerical calculations. The same value $\Gamma_{\mu}$ ($\Gamma_{np}$) has been assigned to all exciton (vibron) states.

| Parameter | Value |
|-----------|-------|
| $m_e/m_0$ | 0.12  |
| $m_h/m_0$ | 0.45  |
| $E_g$ (eV) | 1.865 |
| $\omega_L$ (cm$^{-1}$) | 213.1 |
| $\omega_T$ (cm$^{-1}$) | 165.2 |
| $\beta_L$ ($10^3$ms$^{-1}$) | 2.969 |
| $\beta_T$ ($10^3$ms$^{-1}$) | 0.002 |
| $\epsilon_{ao}$ (CdSe) | 9.53  |
| $\epsilon_{a\infty}$ (CdSe) | 5.72  |
| $\epsilon_{b\infty}$ (Glass) | 4.64  |
| $\Gamma_{\mu}$ (meV) | 5     |
| $\Gamma_{np}$ (cm$^{-1}$) | 2     |
| $P^2$ (eV) | 20    |

*aRef. [31].
*bRef. [9].
*cRef. [28].
*dRef. [32].
*eCalculated from the Lydanne-Sachs-Teller relation.
*fRef. [33].
*gRef. [34].

$P^2 = 2|p_{\infty}|^2/m_0$

TABLE II. List of resonance radii and corresponding resonant exciton levels (see text and Fig. 6). The incoming (outgoing) resonances are labeled by IN (ON).

| R (Å) | $N, L$ | - |
|-------|--------|---|
| 18.0  | (1.0)  | O1 |
| 20.3  | (1.1)  | I1 |
| 26.0  | (2.1)  | I2 |
| 27.8  | (3.1)  | I3 |
| 28.0  | (3.0)  | O3 |
| 30.0  | (4.1)  | I4 |
CdSe

(a) $R=16\ \text{Å}$

$\ell_p=1, n_p=1$

$n_p=3$  $n_p=2$

(b) $R=18\ \text{Å}$

$\ell_p=1, n_p=1$

$n_p=3$  $n_p=2$

(c) $R=21\ \text{Å}$

$\ell_p=1, n_p=1$

$n_p=4$  $n_p=3$  $n_p=2$

Hyper-Raman Spectrum (a. u.)

Hyper-Raman Shift (cm$^{-1}$)
CdSe

$\bar{R} = 21 \, \text{Å}$

$2\hbar\omega_l = 2.771 \, \text{eV}$

$l_p = 1, n_p = 1$

Hyper-Raman Shift (cm$^{-1}$)

HR Spectrum (a. u.)
CdSe

$2\hbar\omega_l = 2.771$ eV

Hyper-Raman Spectrum (a. u.)

Hyper-Raman-Shift (cm$^{-1}$)

$\bar{R} = 15$ Å

$\bar{R} = 16$ Å

$\bar{R} = 18$ Å

$\bar{R} = 20$ Å

$\bar{R} = 21$ Å

$\bar{R} = 28$ Å