Exciton−LO-phonon interaction in CuCl spherical quantum dots studied by resonant hyper-Raman spectroscopy

A. V. Baranov,* S. Yamauchi, and Y. Masumoto
Institute of Physics, University of Tsukuba, Tsukuba, Ibaraki 305, Japan
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Resonant hyper-Raman-scattering spectroscopy was applied for studies of the exciton–LO-phonon interaction in spherical CuCl nanocrystals of different sizes embedded in a glass matrix. Both the LO and 2LO phonon bands have shown a prominent resonance with the lowest energy $1S$ confined exciton state. The ratio of the integral intensities of the LO and 2LO bands ρ was found to increase with increase of the incident photon energy, or decrease of the nanocrystal radius. The Huang-Rhys factor S has been calculated as a function of the nanocrystal size from the experimentally measured values of ρ on the offset harmonic-oscillator model of electron-vibrational coupling. It has been found that S increases monotonically from 0.22 to 0.7, with the nanocrystal radius decreasing from 3.6 to 1.6 nm. [S0163-1829(97)00840-0]

I. INTRODUCTION

Exciton-phonon interaction is one of the main problems in the physics of the quasi-zero-dimensional semiconductor systems, quantum dots (QD's).[1–8] Three-dimensional confinement drastically changes the interaction itself between the confined excitons and phonons. In this context the so-called phonon ''bottleneck'' effect[9] and the size dependence of the interaction have attracted much attention. A lot of experimental and theoretical efforts have been made to investigate this problem mainly for QD's in the strong confinement regime.[1–4,10–16] Surprisingly, there are a few studies dealing with exciton–LO-phonon coupling mediated by the Fröhlich interaction for polar semiconductor QD's in the weak confinement regime.[5–8] The results of theoretical considerations differ from each other: Marini, Stebe, and Kartheuser,[5] who accounted for Coulomb interaction between an electron and a hole in the model of a donorlike exciton located at the center of the CuCl spherical nanocrystal, have concluded that the Huang-Rhys factor S decreases with decrease of the nanosphere radius R, reaches a minimum value of 3.1 at $R/R_B \approx 3.3$, and increases with the further decrease of R, where $R_B = 0.7$ nm is the bulk exciton Bohr radius. In contrast, in the model of interaction between confined free-exciton and LO modes of angular momentum $l = 0$, Fedorov and Baranov[7] have predicted that S for CuBr QD's increases monotonically by two orders of magnitude and reaches a maximum value of 1.5 as R/R_B decreases from 9 to 1.2. Recent photoluminescence experiments[6,8] showed that exciton–LO-phonon interaction, most likely, increases with a decrease of the nanocrystal size. It results in the appearance of the exciton polaron and exciton-phonon complexes in CuCl dots,[6] and strongly coupled exciton-phonon states in CuBr dots[8] when the ratio R/R_B decreases down to 2.5–3. Nevertheless, numerical evaluations of the matrix elements of the exciton–LO-phonon coupling have not been done from these experimental data.

Resonant Raman scattering (RRS) spectroscopy has been widely used to study semiconductor QD's beginning from a pioneering work of Rossetti, Nakahara, and Brus.[17] In particular, for Cd(S,Se) (Refs. 2, 3, 13, and 15) and PbS (Ref. 16) nanocrystals in the strong confinement regime, the value of the electron–LO-phonon coupling in QD's, and its size dependence have been obtained by the use of the ratio of the overtone and fundamental bands in the RRS spectra. It was shown that in QD's with a discrete set of energy levels the RRS by LO phonons can be described by the theory of RRS, which was well developed for molecules in the case of resonance with strongly allowed transition (the Albrecht A term).[18,19] The values of the Franck-Condon factors which determine the Raman band intensities were found on the basis of the offset harmonic-oscillator model of electron-vibrational coupling.[20] Then the relative intensity of the second-order Raman band (I_2) with respect to that of the first-order band (I_1), $\rho = I_2/I_1$, increases with the growth of the dimensionless displacement of the harmonic-oscillator potentials in ground and excited states Δ, and, generally, decreases with the increase of the homogeneous width of the excited state Γ. For the Fröhlich interaction with one LO-phonon mode, the relation[21] $S = \Delta^2$ between the Huang-Rhys factors S and Δ was used to calculate the former from the experimental values of ρ under reasonable assumptions for values of Γ.[2,13,16] At the same level of approximation this model can be applied to the RRS by LO phonon in spherical QD's in the weak or intermediate confinement regimes, where the lowest-energy confined exciton state, $1S$, is in resonance with the incident photons. Nevertheless, such measurements for CuCl or CuBr QD's systems are not known to us. Secondary radiation spectra of the CuCl dots excited in resonance with $1S$ confined Z_3 exciton state,[6] show the LO-phonon band, but the 2LO-phonon one was not clearly resolved due to overlapping by strong luminescence bands.

At the same time, analogous information about exciton-phonon coupling in QD's can be obtained by using resonant hyper-Raman scattering (RHRS) spectroscopy. Indeed, in Refs. 22 and 23 it was shown that the RHRS cross section is described by the expression analogous to the Albrecht A-term of RRS in two-photon resonance with the electronic state of a molecule, which is strongly allowed for both the

one- and two-photon transitions. A dipole matrix element of the one-photon transition is replaced by the composite matrix element of a two-photon transition between the same electronic states in corresponding expression. Then the same vibrational modes should be observed in both the RHRS and RRS spectra, and intensities of the RHRS bands are determined by the same overlap integrals as those of the RRS bands.

Both one- and two-photon transitions from the ground state to the lowest-energy $1S$ confined Z_3 exciton state are allowed in CuCl QD's due to T_d symmetry.[24] Therefore it is reasonable to apply the molecular theory of RHRS to extract information about the value and size dependence of the $1S$ exciton–LO-phonon coupling from the ρ size dependence.

In this paper we report the results of RHRS studies of spherical CuCl nanocrystals of different sizes embedded in a glass matrix. Both the LO and 2LO RHRS bands have been observed with excitation profiles which agree with that of the two-photon excited resonance luminescence and, therefore, show a prominent resonance with the lowest-energy $1S$ confined exciton state.[25] The ratio of the integral intensities of the LO and 2LO bands ρ was found to increase with increase of the incident photon energy, or decrease of radius of the nanocrystals. Analysis of the expressions for the intensities of the first- and second-order RHRS derived in the framework of the offset harmonic-oscillator model of exciton-vibrational coupling with one LO mode showed that the Huang-Rhys factor S can be related to ρ by the simple relation $S = 2\rho$ when the homogeneous width of the resonant state Γ is much less than the LO-phonon energy, and when the nanocrystal size dispersion is narrow enough. It has been found that S, thus defined, increases monotonically from 0.22 to 0.7, with the nanocrystal radius decreasing from 3.6 to 1.6 nm.

II. EXPERIMENTS AND RESULTS

CuCl nanocrystals were grown in a borosilicate glass matrix. The mean radius of the nanocrystals in five different samples were estimated to be 1.8, 2.0, 2.2, 2.9, and 3.6 nm by means of small-angle x-ray scattering. The plates of the specimens with a thickness of 0.25 mm were directly immersed in superfluid helium at 2 K. The RHRS spectra were taken under the excitation of the $1S$ confined state of the Z_3 exciton by pulsed radiation from a frequency-tunable Ti-sapphire laser pumped by a 3-kHz Q-switched Nd^{3+}:YAG laser (where YAG denotes yttrium aluminium garnet). The experiment was performed in the $z(yy,\text{unspecified})z$ incident-scattered light geometry (Porto's notation). Secondary radiation from the sample was dispersed with a single-grating monochromator equipped with a liquid-nitrogen-cooled charge-coupled-device detector. A spectral resolution of 1 meV was adopted. The experimental setup and the measurement procedures are similar to that used in Ref. 25.

As already shown in Ref. 25, two-photon excited light emission spectra of CuCl QD samples contain two sets of bands which differ from each other by their Stokes shift and by excitation profiles, except for the line of the resonant luminescence (RL) whose energy just equals twice the incident photon energy. One set contains two lines which have constant Stokes shifts equal to the energies of the LO and
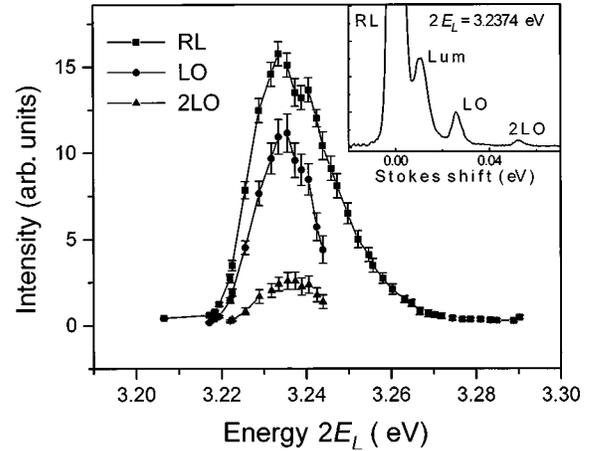
FIG. 1. Two-photon excitation profiles of the RL, LO and 2LO bands for CuCl nanocrystals with a mean radius of 2.2 nm. The inset shows the spectrum of two-photon excited light emission containing resonant luminescence (RL), luminescence (Lum), and RHRS bands (LO and 2LO); the value of twice the incident photon energy $2E_L$ is shown.

2LO phonons in the bulk CuCl (25.6 and 52 meV, respectively), and can be assigned to the RHRS or phonon-assistant hot luminescence. Several lines belonging to another set have Stokes shifts that increase with the increase of the incident photon energy and different excitation profiles. These are attributed to luminescence due to the annihilation of the exciton in the lowest-energy state excited through the higher-energy confined exciton states.[25] The inset of Fig. 1 shows a typical example of the coexistence of the RHRS bands and one of those luminescence bands. Unlike one-photon excitation spectroscopy,[6] no distinguished signal which may be assigned to the TO phonon was observed. In this study we have concentrated on behaviors of the LO and 2LO RHRS bands. In order to determine the resonant exciton state which contributes mainly to RHRS by LO phonons, we compared the excitation profiles of the LO and 2LO bands with that of the resonant luminescence from two-photon excited $1S$ confined exciton state,[25] because the excitation profile of RL reflects a size distribution of the nanocrystals. In Fig. 1 we show that the LO and 2LO band excitation profiles agree with the RL one, and within the experimental error their maxima practically coincide with each other for a sample with a nanosphere mean size of 2.2 nm. The same statement holds for the other samples studied. This means that in this region of the excitation energy the two-photon resonance with $1S$ confined exciton states dominates the RHRS by LO-phonon process. All the measurements of the integral intensities of the LO- and 2LO-phonon bands in the RHRS spectra discussed in this work have been done at these excitation conditions. Figure 2 shows examples of the RHRS spectra of different samples excited at different energies, and results of the fitting of the LO- and 2LO-phonon bands by two Gaussians (the low-energy tail of the RL or luminescence lines was described by an exponential function). All the spectra are corrected for reabsorption of the emitted light. Figure 3(a), where the values of ρ thus measured for five samples are shown as a function of twice the incident phonon energy,
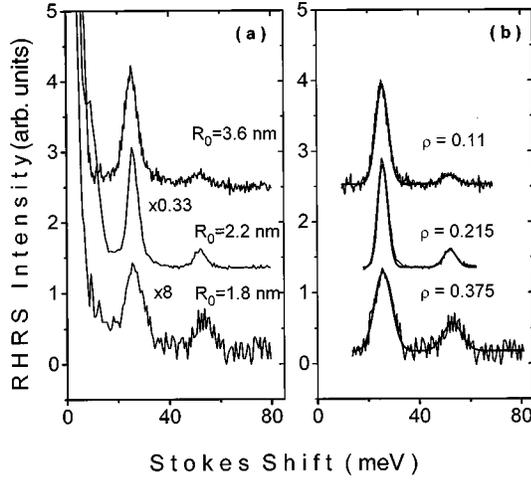
FIG. 2. (a) Representative set of the RHRS spectra of CuCl nanocrystals with different mean radii. For clarity, the spectra are shifted vertically. Twice the incident photon energies $2E_L$ are 3.2145 eV (top), 3.2235 eV (middle), and 3.2570 eV (bottom). The RHRS amplitudes were multiplied by the factor shown. (b) Results of the fitting of the LO and 2LO bands in the same spectra by two Gaussians. Ratio of the integral intensity of the 2LO band to that of the LO band, ρ, is shown.

demonstrates clearly that ρ increases with an increase of the excitation energy.

III. DISCUSSION

In the low-temperature limit ($T=0$ K) the expression for the cross section of the n LO-phonon RHRS process in a single CuCl QD can be easily derived from Ref. 22 (see the Appendix), and written in the form

$$\sigma_{0 \to n}(E_L) = C \times |M_{GS}|^2 |M_{2,SG}|^2$$
$$\times \left| \sum_{s=0}^{\infty} \frac{\langle n|s \rangle \langle s|0 \rangle}{E_{1S} + s\hbar\omega_{LO} - 2E_L - i\Gamma_s} \right|^2, \quad (1)$$

where C is the constant, M_{GS} and $M_{2,SG}$ are the adiabatic matrix elements of the dipole one-photon transition and the composite matrix element of the dipole two-photon transition between the ground state G and pure confined exciton state $1S$, respectively. Both $|M_{GS}|^2$ and $|M_{2,SG}|^2$ are proportional to R^3; $\langle n|s \rangle$ and $\langle s|0 \rangle$ are the Franck-Condon integrals between the intermediate vibrational levels of the $1S$ state $|s \rangle$, and initial $|0 \rangle$ and final $|n \rangle$ vibrational levels of the G state of the QD; E_{1S} is the size-dependent energy of the $1S$ exciton transition; $\hbar\omega_{LO}$ and E_L are the energies of the LO phonon and the incident photon, respectively; and Γ_s is the homogeneous width of the intermediate state s. Here we consider a two-photon resonance with an isolated exciton transition, and suppose that other exciton states which can be considered as intermediate ones in the RHRS process are far from the resonant exciton state.

It is seen from Eq. (1) that the value of the RHRS cross section is determined by the values of the one-dimensional Franck-Condon factors similarly to RRS.[2] The products of overlap integrals needed to calculate the first- and second-order RHRS band intensities are[18]
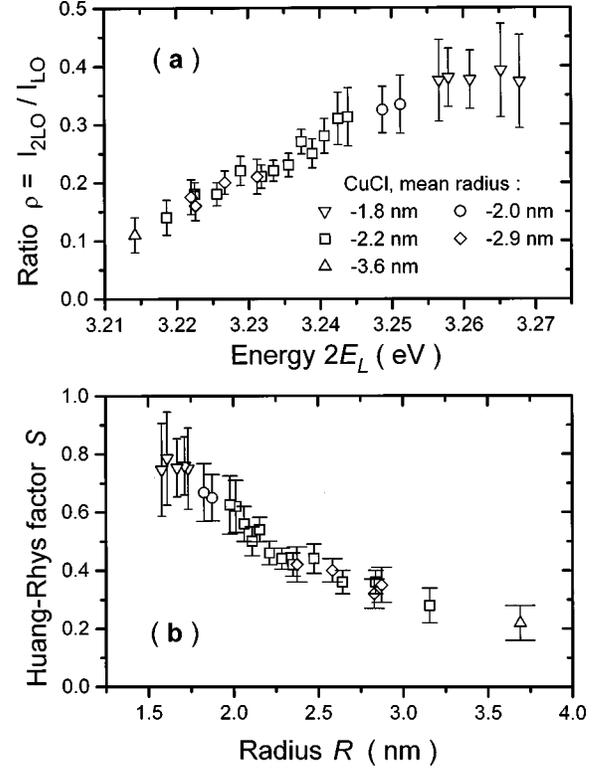
FIG. 3. (a) The ratio of the second-order to first-order RHRS bands ρ as a function of twice the incident photon energy $2E_L$ measured for the five samples with different mean sizes of the nanocrystals. (b) The corresponding size dependence of the Huang-Rhys factor S was calculated by taking into account the size-selective origin of the RHRS spectra (see the text).

$$|\langle 0|s \rangle||\langle s|0 \rangle| = |\langle s|0 \rangle|^2 = \exp(-\Delta^2/2)(\Delta^2/2)^s/s!, \quad (2)$$

$$|\langle 1|s \rangle||\langle s|0 \rangle| = \sqrt{2}[(s-\Delta^2/2)/\Delta]|\langle s|0 \rangle|^2, \quad (3)$$

$$|\langle 2|s \rangle||\langle s|0 \rangle| = \sqrt{2}\{[(s-\Delta^2/2)^2 - s]/\Delta^2\}|\langle s|0 \rangle|^2, \quad (4)$$

where Δ is the dimensionless displacement; $\Delta^2 = S$ for the Fröhlich interaction with one LO-phonon mode. The problem of evaluating Δ by using experimental intensities of the first- and second-order RHRS bands reduces now to the problem of summing over excited vibrational states s in Eq. (1). Because the fumdamental and overtone intensities depend on the homogeneous width of each intermediate state Γ_s, ρ depends on Γ_s.

Then, assuming a randomly oriented nanocrystals with radius R, the total radiated power resulting from the n-phonon RHRS integrated over all direction and polarizations of the scattered light is given by

$$P_{0 \to n}(E_L, R) = N\sigma_{0 \to n}(E_L, R)I^2, \quad (5)$$

where I is the incident photon flux and N is the number of the nanocrystals in the scattering volume.

The particle size dispersion in samples should be taken into account by the integration of Eq. (5) over the nanocrystal size distribution,

$$P_{0 \to n}(E_L) = \int \sigma_{0 \to n}(E_L, R) f(R) dR, \qquad (6)$$

where $f(R)$ is the normalized size distribution function, e.g., the Gaussian function. This integration is not simple due to the unknown size dependence of $\Delta(R)$. However, in the case that $\Gamma_s \ll \hbar \omega_{LO}$ holds, and that the levels s for nanocrystals of definite sizes are resonantly excited, contributions from neighboring levels $s \pm 1$, etc., are negligible, and we can reduce Eq. (6) to

$$P_{0 \to n}(2E_L = E_{1S} + s\hbar\omega_{LO}) \propto \sum_{p=0}^{\infty} N^p \times R_p^6$$
$$\times \left| \frac{1}{\Gamma_p} \langle n|p\rangle \langle p|0\rangle \right|^2, \quad (7)$$

where N^p is the relative number of the nanocrystals with radius R_p which interact resonantly with light of $2E_L = E_{1S} + p\hbar\omega_{LO}$, $p = 0, 1, \ldots, s \ldots$. If the size distribution function is narrow enough, i.e., if the width of the inhomogeneously broadened two-photon absorption band is less than $\hbar\omega_{LO}$, or if experimental measurements are carried out in such way that $N^{p-1}, N^{p+1} \ll N^p$, the sum in Eq. (8) contains only one term. Then for the two-photon resonance with the pure exciton transition, $E_{1S}(R) = 2E_L$ and $p = s = 0$, the value of ρ is simply derived from Eqs. (2)–(4) and (7):

$$\rho = \Delta^2/2 = S/2. \qquad (8)$$

Now let us show that expressions (1)–(8) can be used for the systems under study. (i) Fröhlich interaction governs RHRS in CuCl OD's, since only the LO and 2LO bands are observable in the spectra. (ii) Excitation profiles of the LO- and 2LO-phonon bands demonstrate that two-photon resonance with pure $1S$ confined exciton state contributes mainly to the intensity of these bands. (iii) Last hole burning[26] and photon echo[27] experiments show that for CuCl nanocrystals of ≈ 2 nm embedded in a glass matrix the homogeneous width Γ_0 of the $1S$ confined exciton is not greater than 0.2 meV at 2 K and, hence, is much less than the LO-phonon energy of 25.6 meV. Our estimations showed that we can consider the CuCl QD's as an effective two-level system with well separated vibronic resonances, even if $\Gamma_1 = 10\Gamma_0$. (iv) Widths of the RL excitation profiles inhomogeneously broadened due to particle size dispersion are slightly smaller than the LO-phonon energy. Because of this, the measurements of the LO and 2LO band intensities were performed for the RHRS spectra excited at near maxima or at low-energy parts of the RL excitation profiles. In this case a contribution of the two-photon resonant vibrational level $s = 1$ of the nanocrystals of larger size is not important. Then we can use relation (8) for a rough evaluation of S. The value of S thus defined varies monotonically from 0.2 to 0.75 in the region of the change of the nanocrystal size. Now, we can approximate the S size dependence by a straight line, and calculate a possible contribution of the off-resonant nanocrystals to the intensities of the LO- and 2LO-phonon bands for each sample by the use of relations (1) and (6), with $s = 0$ and $\Gamma_0 = 0.2$ meV, a Gaussian type of particle size dispersion, and a well-known relation between the radius of QD's and 1S exciton energy

$$E_{1S}(R) = E_B + \frac{\hbar^2 \pi^2}{2MR^2}, \qquad (9)$$

where $E_B = 3.2022$ eV is the bulk energy of the $1S$ Z_3 exciton with a translational mass M of $2.3m_0$ (m_0 is the free-electron mass). Our calculation showed that this contribution is not more than 15% and, hence, that the nanocrystals for which relation $2E_L = E_{1S}$ holds contribute mainly to the intensities of the RHRS bands; i.e., in our case RHRS is a sort of size-selective spectroscopy. In Fig. 3(b) the Huang-Rhys factor $S = 2\rho$, plotted as a function of the CuCl spherical nanocrystal radius calculated with formula (9), demonstrates a pronounced increase with a decrease of the nanocrystal radius.

This result supports qualitative conclusions about the size dependence of exciton–LO-phonon coupling based on photoluminescence studies of CuCl (Ref. 6) and CuBr (Ref. 8) QD's in analogous confinement regimes. The size dependence of the Huang-Rhys factor for CuCl QD's is also in qualitative agreement with the theoretical prediction of Ref. 7 for CuBr QD's, although a quantitative discrepancy, especially pronounced for nanocrystals of greater sizes, is not quite clear to us. One of the possible reasons is that the Huang-Rhys factor does not describe a whole exciton-phonon coupling in QD's in the weak confinement regime. A contribution of the off-diagonal Fröhlich interaction involving intraband exciton transitions, which dominates this interaction in a perfect bulk,[28] is expected to be more pronounced with an increase of the particle size.[7] Another reason for the discrepancy may be an oversimplification of our models, which does not take into account the optical modes with different angular momenta. The increase of S with a decrease of the nanocrystal radius of QD's in the weak and intermediate confinement regimes qualitatively contradicts the conclusions of Ref. 5. This is probably due to the fact that donorlike properties of the confined exciton are negligible for CuCl nanocrystals embedded in a glass matrix.

APPENDIX

Assuming randomly oriented scattering centers, the total radiated power resulting from a hyper-Raman transition from the molecular vibrational state $|i\rangle$ to the state $|f\rangle$, integrated over all direction and polarizations of the scattered light, is given by

$$P_{i \to f}(E_L) = I^2 \sigma_{i \to f}(E_L), \qquad (A1)$$

where I is the incident photon flux and $\sigma_{i \to f}(E)$ is the cross section of the hyper-Raman scattering[29]:

$$\sigma_{i \to f}(E_L) = \frac{8E_L E_S^3}{3c^3\hbar^2} \left| \sum_{\rho\sigma\tau} e_S^\rho \beta_{i \to f}^{\rho\sigma\tau}(E_L) e_L^\sigma e_L^\tau \right|^2, \quad (A2)$$

where E_L and E_S are the incident and scattered photon energies; e_S^ρ and e_L^σ, e_L^τ are the unit polarization vectors of the

scattered and incident light, respectively; $\rho, \sigma, \tau = x, y, z$ are the Cartesian coordinates tied to the molecule; and $\beta_{i \to f}^{\rho \sigma \tau}(E_L)$ is the quadratic polarizability of the system. In the case of two-photon resonance with an electronic state transition which is strongly allowed for both one- and two-photon pro-

cesses, the component of the hyperpolarizability tensor $\beta_{i \to f}^{\rho \sigma \tau}(E_L)$ can be described in the framework of the Condon approximation by an expression which is completely analogous to the Albrecht A term in RRS,[22] and can be rewritten in the form

$$\beta_{i \to f}^{\rho \sigma \tau}(E_L) = \frac{1}{\hbar^2} \sum_{R,r} \sum_{S,s} \frac{M_{GS}^{\rho} M_{SR}^{\sigma} M_{RG}^{\tau} \langle f|s\rangle \langle s|r\rangle \langle r|i\rangle}{[E_{GS} + (s-i)\hbar\Omega - 2E_L - i\Gamma_s][E_{GR} + (r-i)\hbar\Omega - E_L - i\Gamma_r]}, \tag{A3}$$

where G and R and S are the ground and two intermediate electronic states, respectively; $|i\rangle$ and $|f\rangle$ are the vibrational levels of the G state, and $|r\rangle$ and $|s\rangle$ are those of the R and S states, respectively; M_{JK}^i is the ith component of the adiabatic matrix element of the dipole transition between the electronic states J and K separated by the energy gap E_{JK}; $\langle j|k\rangle$ is the Franck-Condon integral between the vibrational states $|k\rangle$ and $|j\rangle$; $\hbar\Omega$ and E_L are the energies of the phonon and the incident photon, respectively; and Γ_j is the homogeneous width of the intermediate vibrational level j.

Since only the vibronic states of the resonant electronic state (S) are considered, and it is supposed that $E_{GR} + (r - i)\hbar\Omega \gg E_L$, we can omit the sum over S and R, and use closure to remove the sum over r: $\sum_r \langle s|r\rangle \langle r|i\rangle = \langle s|i\rangle$, i.e., we replace the set of the intermediate states R and r by an effective electronic state R with constant matrix elements of the dipole one-photon transitions

M_{SR}^{σ} and M_{RG}^{τ}. Then the product $M_{SR}^{\sigma} M_{RG}^{\tau}[E_{GR} + (r - i)\hbar\Omega - E_L - i\Gamma_r]^{-1} \equiv M_{2,SG}^{\sigma\tau}$ can be considered as a composite matrix element of the dipole two-photon transition between the ground G and resonant S states, where the last term is independent of E_L. Finally, we eliminate the sum over the ρ, σ, and τ indices in Eq. (A2), supposing that a set of axes is chosen such that only one component of M_{JK}^i is nonzero.

Then in the low-temperature limit ($i \equiv 0$, $f \equiv n$), the expression for the n-phonon RHRS cross section for the two-photon resonance of the incident light with the vibronic levels of the lowest energy electronic state becomes

$$\sigma_{0 \to n}(E) = \text{const} \times |M_{GS}|^2 |M_{2,SG}|^2$$

$$\times \left| \sum_{s=0}^{\infty} \frac{\langle n|s\rangle \langle s|0\rangle}{E_0 + s\hbar\omega_{LO} - 2E - i\Gamma_s} \right|^2. \tag{A4}$$

*Permanent and present address: S. I. Vavilov State Optical Institute, 199034, St. Petersburg, Russia.

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