Anomalous features of resonant hyper-Raman scattering in CuBr quantum dots: Evidence of exciton-phonon-coupled states similar to molecules

K. Inoue, A. Yamanaka, and K. Toba
Research Institute for Electronic Science, Hokkaido University, Kita-ku, Sapporo 060, Japan

A. V. Baranov, A. A. Onushchenko, and A. V. Fedorov
Vavilov State Optical Institute, Birgebirya Liniya 14, St. Petersburg, Russia

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A resonant hyper-Raman scattering signal has been successfully observed in CuBr quantum dots of a weak-confinement regime. It is found that up to fifth-order LO-phonon scattering signals appear in a two-photon resonance with the lowest confined state of the Z_{12}, S exciton, and that the observed order N depends on the two-photon energy $2\hbar\omega_i$ for the excitation in such a way that it conforms to the equation $N \leqslant (2\hbar\omega_i - E_{\mathrm{edge}})/\hbar\omega_{\mathrm{LO}}$, with $\hbar\omega_{\mathrm{LO}}$ and E_{edge} being energies of the LO phonon and the absorption edge, respectively. The anomalous result observed indicates that coupled states of the Wannier exciton and the LO phonon are rather good elementary excitations in these dots. [S0163-1829(96)51836-9]

Semiconductor nanocrystals or quantum dots (QD's) having a radius R_0 comparable to the bulk exciton Bohr radius r_B have been intensively studied since the first experimental[1] and theoretical[2] works were reported. Depending on a relative magnitude between R_0 and r_B, they may be classified into two regimes; for $R_0 \gg r_B$, a weak-confinement regime where the exciton center-of-mass momentum is quantized, and for $R_0 \ll r_B$, a strong-confinement one where the momenta of the electron and the hole are separately quantized. In both cases the characteristics of electronic states are of great interest. As any elementary excitations such as phonons are also confined, interactions of the electron or the exciton with other quasiparticles are expected to have a new aspect. Although a number of experimental works have been done up until now, the nature of the electronic structure is not yet well understood. One reason for this is that the quality of samples available at present is not good enough. Namely, the sample or the quantum-dot system has a dot-size distribution causing a large inhomogeneous broadening, as is typically seen in the one-photon absorption (OPA) spectrum.

In order to clarify the electronic structure, we performed an experiment of resonant hyper-Raman scattering (RHRS) for a CuBr QD system, which is representative of the weak-confinement regime; the average dot radius of 3.2 nm is more than two times larger than the bulk r_B value of 1.3 nm. The observed features are rather anomalous, but are still simple. As a result, we report that exciton-phonon coupled states are well-defined elementary excitations inherent in these dots. This is interpreted as being caused by a strong coupling of the Wannier exciton and LO phonon due to the confinement effect. The hyper-Raman scattering (HRS) by an optic phonon is such that two incident photons with each photon of $\hbar\omega_i$ in energy are incoherently scattered by a phonon with $\hbar\omega_p$ energy, creating a new photon of $\hbar\omega_s$. Resonant phenomena[3] of HRS can be observed when $2\hbar\omega_i$ (ingoing) or $\hbar\omega_s$ (outgoing resonance) is resonant in energy with one of the excited states. Consequently, the selection rules are different between RHRS and resonant Raman scattering (RRS). The detailed selection rules, however, depend on the character of the electron-phonon interaction. In a simple case, the RHRS spectroscopy provides a complementary tool[4] to two-photon absorption (TPA) spectroscopy for exploring the electronic structure of a solid-state substance. It is known that the QD samples available at present, in particular, those of CuCl and CuBr QD's more or less suffer serious problems such as photodarkening, photobleaching, persistent hole burning, and others, when illuminated in the exciton absorption region. Accordingly, one-photon excitation spectroscopy with the use of relatively intense light makes the situation complicated. In this respect, the RHRS spectroscopy is very suited because the sample is transparent to the incident photon, and therefore should be free from suffering those problems.

CuBr nanocrystals were embedded in a multicomponent silicate glass matrix at 0.1% by weight. The samples were obtained by using the diffusion phase decomposition of a supersaturated solid solution of CuBr-doped glass under secondary heat treatment. The size distribution of the crystallites for this case is known to be well described in terms of the Lifshitz-Slesov model.[5,6] The average radius of 3.2 nm was determined by small-angle x-ray-diffraction measurement. A plane-parallel plate specimen with a thickness of 0.25 mm was prepared. In Fig. 1(a), the observed OPA spectrum at 2 K is shown. The lowest and second-lowest energy peaks are attributed to Z_{12} and Z_3, S excitons with confinement quantum numbers of $n=1$ and $l=0$ (l: angular momentum), respectively, and their spectral widths are broadened by size distribution. A pronounced shift of the energy E_1 of the Z_{12} exciton of $n=1$ and $l=0$ due to size confinement, from the bulk value 2.968 eV can be clearly seen.

The RHRS signals were excited by using a repetitively pulsed output beam from a frequency-tunable Ti-sapphire laser. The typical characteristics are a peak power of 1 kW and a pulse width of 40 ns when operated at a repetition rate of 3 kHz. An average power of less than 100 mW was used. The laser frequency was varied from 1.475 to 1.630 eV for

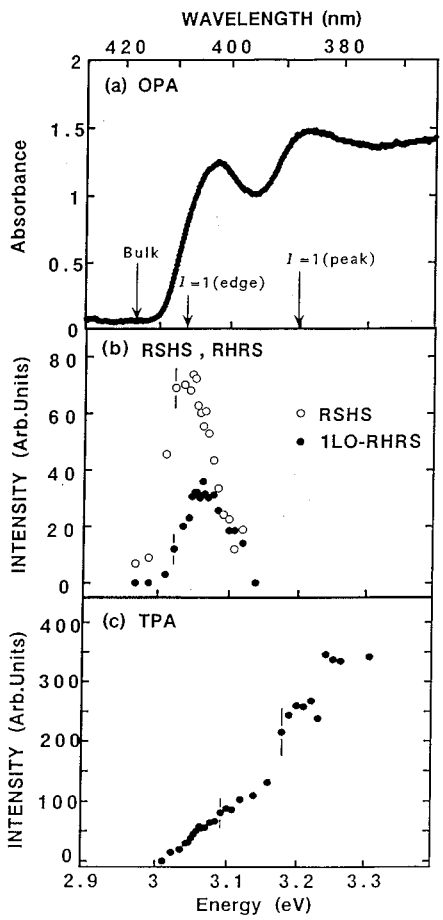

FIG. 1. Comparison of the relevant spectra observed at 2 K for a CuBr quantum-dot sample embedded in a glass matrix with an average radius of 3.2 nm. (a) The one-photon absorption spectrum (OPA) at 2 K: the energy position of the Z_{12},S exciton for bulk CuBr is marked by an arrow. For other two arrows, see the text. (b) Two-photon excitation spectra of RSHS and one-LO HRS scattering signals. (c) TPA.

twice the photon energy $2\hbar\omega_i$ to sweep through the energy regions of the Z_{12} and Z_3, S excitons of $n=1$ and $l=0$, as shown in Fig. 1(a). It is noted that both one-photon and two-photon transitions to those exciton states are allowed in the electric dipole approximation as is the case for bulk CuBr.[7,8] The laser beam was focused by a lens with a focal length of 5 cm onto a specimen cooled to 2 K in a helium cryostat. Radiation scattered in a quasiforward direction was collected by a lens, dispersed with the use of a single-grating monochromator with an inverse dispersion of 29 A/mm, and then detected by a cooled optical multichannel detector. A spectral resolution power of 25 cm^{-1} was adopted.

Figure 2 shows examples of the RHRS spectrum for several incident photon energy. A broad spectral line is discernible and is ascribed to an emission or fluorescence due to the annihilation or recombination of the exciton at the band edge,[9] since it has a fixed peak energy independent of excitation wavelength. A spectral line at $2\hbar\omega_i$ is a second-harmonic scattering (RSHS) signal,[10] which also emerges in two-photon resonance with an excited electronic state. At an excitation of 1.511 eV, a RHRS signal with a broader spectral width than that of the RSHS signal is clearly discernible.

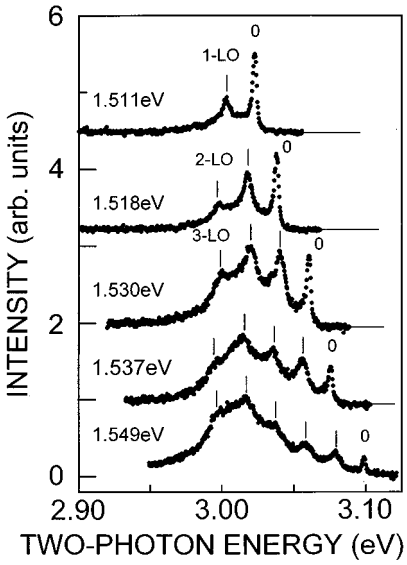

FIG. 2. Examples of the resonant hyper-Raman scattering signal at 2 K in a CuBr quantum-dot sample for several excitation photon energies. The line at $2\hbar\omega_i$ marked by ''0'' in each spectrum is the resonant second-harmonic scattering signal, and the signals located apart by multiple of the LO-phonon energy from $2\hbar\omega_i$ are resonant hyper-Raman scatterings or hot luminescences. A broad spectrum with the center energy independent of excitation photon energy is a luminescence due to recombination of bound exciton at the band edge of the OPA spectrum.

The energy shift of 20.2 meV from the RSHS signal is almost the same as with the LO-phonon energy for bulk CuBr, 21.5 meV,[11] indicating that the spectral line is a HRS by LO phonon in origin. It is noted that this one-LO-phonon signal disappears when twice the excitation photon energy $2\hbar\omega_i$ is further away from the lower edge energy E_{edge} of OPA, indicating that it is a resonant signal. On the other hand, as $2\hbar\omega_i$ increases from the edge, higher-order HR signals noticeably manifest themselves up to five LO phonons [hereafter referred to as (a)].

The major experimental results other than the above (a) are summarized as follows. (b) The relative intensity of Nth LO-phonon signal does not appreciably diminish even if the order of N increases. (c) The intensity of the RSHS signal is of the same order of magnitude as that of the one-LO-RHRS signal in all cases. (d) Significantly, higher-order signals appear on such an order N as to fit the equation $N \leqslant (2\hbar\omega_i - E_{\text{edge}})/\hbar\omega_{\text{LO}}$ (up to $N=5$), where $\hbar\omega_{\text{LO}}$ refers to the LO-phonon energy. (e) All signals from $N=0$ to 5 with the RSHS signal being regarded as zero-phonon signal, disappear when $2\hbar\omega_i$ exceeds the one-photon absorption region due to the Z_{12},S exciton. (f) A close correlation is recognized between the excitation spectra of RSHS and one-LO-phonon signals, as is shown in Fig. 1(b), where they appear to be a replica of the OPA spectrum due to the Z_{12},S exciton, aside from slight deviation between respective peak energies. (g) On the other hand, no clear-cut correlation is recognized between those spectra and the observed TPA spectrum [Fig. 1(c)], which exhibits a monotonous increase with the increase of $2\hbar\omega_i$: the TPA spectrum was obtained by utilizing the intensity of the broad edge emission as a probe. (h) The signals were observed with

incident average power similar to a typical case of Raman scattering (RS). This fact is very surprising because the HRS arises from a process of higher order than RS with respect to incident power.

Now, let us interpret the anomalous features described above. First of all, we point out that the present spectroscopy provides a size-selective one in which incident laser excites only a small amount of particular dots with the exciton energy coincident with $2\hbar\omega_i$ within their homogeneous spectral widths. Most importantly, if we focus on the OPA region below 3.13 eV due to the $Z_{12}S$ exciton, only where both RSHS and RHRS signals are observed, each particular dot thus selected has only one or at most two discrete confined exciton states, one the Z_{12},S exciton of $n=1$ and $l=0$ and the other of $n=1$ and $l=1$. The latter second-lowest energy position E_2 of the Z_{12} exciton is marked in Fig. 1(a) for the dots with the relevant sizes corresponding to E_{edge} (the largest size) and the peak energy of the OPA spectrum, respectively; E_2 is estimated by using the equation for spherical dots, $E_2-E_1=[(4.49/\pi)^2-1]E_{\text{ob}}$, where E_{ob} represents the observed value of the confinement energy for the Z_{12}, S exciton of $l=0$. Taking this into consideration, facts (a)–(c) indicate that perturbation theory taking pure exciton states as unperturbed base functions and exciton-phonon interaction as perturbation may not apply to the present system, and that for the present dots strongly coupled states of Wannier exciton and LO phonon are elementary excitation with a good quantum number. It is almost evident that all features from (a) to (h) can be explained well by invoking this vibronic model[12,13] with the help of the Franck-Condon process in a similar way to that of the well-known case of small molecules. Namely, successive (cascading) real transitions between those vibronic states, followed by hot luminescences (HL) should be responsible for the mechanism, rather than virtual transitions in the RHRS process: we use the terminology of HL for simplicity since the distinction[13] between HL and RRS (or RHRS) is not clear, depending on their definitions, while real or virtual transition makes sense. We point out that, in gaining insight into the mechanism, we can take full advantage of information concerning the RSHS or zero-phonon HL, which may be difficult in the case of RRS.

Let us discuss the validity of the above interpretation in more detail. First, considering that TPA actually takes place (g), the seemingly surprising feature of item (b) is reasonable: TPA to the exciton-LO-phonon coupled states as well as the pure exciton is allowed. The observed facts from (a) to (d) are almost self-evident. The reason for item (e) may be as follows. Higher vibronic states for each dot size more or less degenerate or mix in energy with the Z_3 exciton and also, in some cases, other quantum-confined states, e.g., with $l=1$, of the Z_{12} exciton for the same dot. As a result, decay channels to these states give rise to a remarkable decrease of transition to the lower vibronic state, which causes disappearance of all signals in question. This seems to be consistent with the fact that the respective energy differences, 125 meV between the Z_{12} and Z_3 excitons [see Fig. 1(a)] and 110 meV (calculated) between the discrete Z_{12},S-exciton states ($n=1$) of $l=0$ and 1, correspond roughly to six- and five-LO-phonon energies, respectively: both of the energy differences are estimated for the dot at the peak energy of OPA. Also notice that TPA increases monotonously (g), which

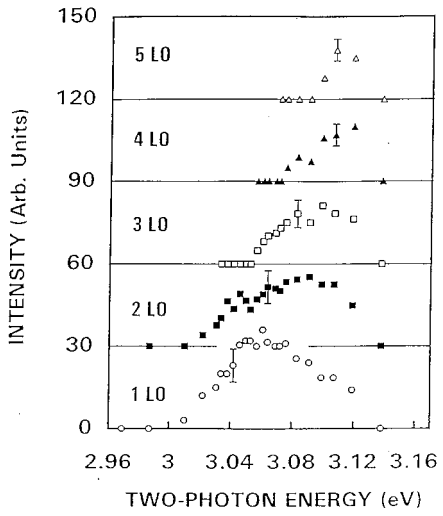

FIG. 3. Comparison of the respective two-photon excitation spectra for one- to five-LO-phonon signals in a CuBr quantum-dot sample. The horizontal axes are shifted relative to each other.

supports the existence of the decay channels described above. In this connection, fact (d) is important, if we consider that the density of states of OPA, or the number of dots, diminishes for such a $2\hbar\omega_i$ as causes the five-LO-phonon spectrum. Again, this indicates that the process is related to the real cascading transitions already described. Finally, it is important to note that the peak energy position of the excitation spectrum for the $(N+1)$th-order LO-phonon signal has a tendency of being higher by $\hbar\omega_{\text{LO}}$ than that of the Nth-order signal, as is shown in Fig. 3. Although the respective peak positions are not very distinct, the data are presumed to provide evidence for the existence of the coupled states described thus far.

Next, one might think that, at first glance, the features of the observed RHRS spectra look like those[14] in RRS for some bulk polar crystals such as CdS, and that therefore the present results are not significantly new. The anomalous phenomenon in[14] CdS that up to nine multiple LO-phonon signals were observed when the continuum band state was excited, has been interpreted as arising from either cascading real[15] or successive virtual transitions,[16–18] from or at a band state in the continuum excited directly by incident photon: in both cases, intraband q-dependent Frohlich interaction is responsible for the process. However, the present situation with only one or two discrete electronic excited states involved is quite different from those of RRS for bulk crystals, as already described. It is important to note that such a multiple LO-phonon structure has not been observed in the latter if discrete exciton states are excited.

Finally, let us discuss the implication of the result. The result implies that the coupling of the exciton and LO phonon in the present dots should become stronger as compared to those with larger sizes and bulk CuBr. To get direct information about this statement, we have also made a similar measurement on two similar samples with larger average radii of 4.3 and 5.2 nm. As a result, we have observed up to fourth- and third-order LO-phonon signals for the former and the latter, respectively: the detailed results, being still under measurement, will be presented in a forthcoming paper.

Therefore the above statement may be supported by those results. Theoretically the problem as to whether the exciton-LO-phonon interaction becomes stronger or weaker as the dot size decreases has been subject to controversy.[19] Two key factors are involved: one is an increasing overlap (local neutrality of the exciton) of electron and hole wave functions with decreasing size, causing a decrease of the coupling strength,[20] and the other is an increasing coupling[19,21] to short-wavelength phonons. Qualitatively, therefore, the present result presumably reflects that the latter contribution is in excess of the former: the magnitude of the coupling strength for a quantitative discussion may be extracted from an analysis based on a model, which will be a future problem. In this connection, a few experimental results have recently been reported for CuCl (Ref. 22), CdS (Ref. 23), and CdS_xSe_{1-x} (Ref. 24) dots which are consistent with our result in the sense that the Frohlich interaction becomes stronger with decreasing size. However, why the Frohlich interaction becomes strong enough in the present case to give rise to such coupled states as causing the higher-order LO-phonon signals is still an open question. Aside from this unsolved problem, we would like to point out that if such a system composed of dots with almost the same radius is developed in the future, the new coupled states clarified in this work would be directly ascertainable by OPA measurement, in which a series of sharp absorption lines should be observed.

In conclusion, rather peculiar results of RHRS or HL were observed in CuBr dots. It is shown that those can be explained well in terms of a model based on the existence of exciton-LO-phonon–coupled states. In this sense the present dots become similar to small molecules. We have also demonstrated that the two-photon resonant spectroscopy provides a powerful tool for exploring electronic structure and electron-phonon interaction in QD's.

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