NQR by Coherent Raman Scattering of a Triplet Exciton in a Molecular Crystal

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Nuclear quadrupole resonance (NQR) of a linear triplet exciton in 1,4-dibromonaphthalene crystals has been observed as coherent Raman scattering. The Br NQR scattering originates from the hyperfine interaction between the electron spin and the Br spins. Since delocalization of the electron spin decreases the interaction, the intensity of the NQR scattering reflects the chain length of the exciton. The exciton is found to be delocalized over about ten molecules, indicating the coherence length of the exciton is limited by scattering due to ^{13}C isomers.

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Heterodyne detection of coherent Raman scattering [1] is a sensitive method to observe coherent excitation in the MHz to GHz range. The typical systems studied so far are sublevel dynamics in atomic vapors and nuclear spin transitions of rare earth ions in ionic crystals [2]. The method should be equally applicable to molecular systems and delocalized excitation. Efforts have been made to extend the frequency up to 14 GHz to study electron spin resonance (ESR) of proteins containing transition metal ions [3]. As a first application to excitons in molecular crystals, we present the detection of the nuclear quadrupole resonance (NQR) of a linear triplet exciton in the crystal of 1,4-dibromonaphthalene (1,4-DBN).

Although the triplet exciton of 1,4-DBN is one of the well-known examples of linear chain excitons, little is known about the chain length of the exciton. It could be deduced from the hyperfine interaction between the electron and nuclear spins. However, the interaction is negligibly small in ESR of the triplet exciton. Observation of the NQR Raman scattering enables us to study the hyperfine interaction of the exciton, because NQR is more sensitive to the interaction than ESR.

The triplet exciton of 1,4-DBN has been studied by optical absorption and emission [4,5], ESR [6], and optically detected magnetic resonance (ODMR) in zero-field [7,8]. ODMR utilizes different decay rates of the triplet sublevels. Microwave transition between the sublevels modifies population distribution, which is optically detected as a change of emission. Because the decay rate does not depend on the nuclear spin, detection of excited state NQR is impossible. The Raman heterodyne method opens the possibility of optical detection of NQR.

The coherent Raman process in a three level system is illustrated in Fig. 1(a). The system is optically excited by a cw laser. The magnetic transition in the excited state is coherently driven by rf irradiation. As a resonant two-photon process, the magnetic coherence is transferred into optical polarization at the sum frequency of the laser and the rf, which produces anti-Stokes Raman field. The resonant forward scattering is detected as a heterodyne beat between the Raman and the laser fields [see Fig. 1(b)]. With the Raman heterodyne method, the Br NQR of the exciton was detected for the first time.

In the monoclinic crystal of 1,4-DBN [9] interaction between translationally equivalent molecules along the c axis delocalizes the triplet excitation to form a linear exciton. Corresponding to the two crystallographically inequivalent sites, there are two exciton bands of the triplet excitation. Figure 2 shows the energy diagram of the system. The bandwidth of the lower exciton is 30 cm^{-1} and the optically allowed $k = 0$ state lies at the bottom of the band [4]. The lifetime of the exciton at liquid helium temperature is about several ms [4,7].

The triplet exciton has three electron spin sublevels. The molecular axes of x, y, and z are shown in Fig. 2. The sublevel x has the longest lifetime. The zero-field ODMR study revealed the x-y transition at 2959 MHz and the x-z transition at 2839 MHz [7]. Because y and z sublevels have similar decay rates, optical detection of the z-y transition at 120 MHz was not successful until microwave double resonance was performed [8]. To observe ODMR signals, amplitude modulation of the microwave had to be much faster than the decay of the exciton, because the spin-lattice relaxation time of the exciton is 3 orders of magnitude shorter than the exciton lifetime [7]. The Br nuclei have $I = 3/2$ so that the

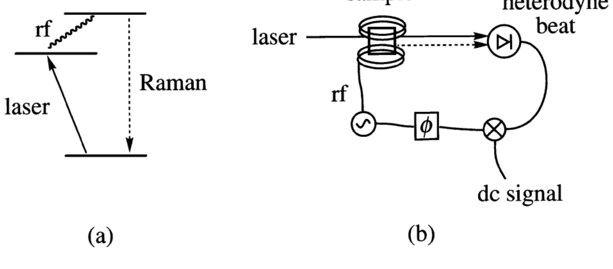

FIG. 1. (a) Coherent Raman process. Anti-Stokes field is generated by laser and rf excitation of a three level system. (b) Optical heterodyne detection of coherent Raman scattering. The laser acts as a local oscillator to produce heterodyne beat with the Raman field. By adjusting phase ϕ of the reference rf, absorptive and dispersive components of the beat signal are obtained.

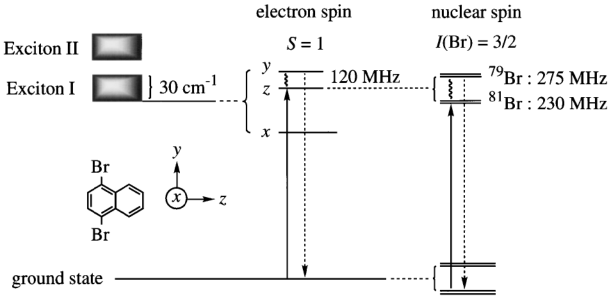

FIG. 2. Triplet excitation in 1,4-DBN crystal. The bottom of the band of the lower exciton was excited in the experiment. The exciton has three electron spin sublevels, which further split by the quadrupole interaction of Br nuclei. Splitting due to one Br nucleus is shown in the figure. The coherent Raman processes of ESR and NQR of the exciton are indicated by arrows.

four nuclear spin levels split into two doublets due to the quadrupole interaction. The splitting in localized triplet monomers is around 270 MHz for ^{79}Br and 220 MHz for ^{81}Br [10].

The crystal of 1,4-DBN was grown by the Bridgeman method. Before the crystal growth the material was extensively zone refined for more than 200 passes. The experimental scheme is shown in Fig. 1(b). A single frequency cw laser with a power of ca. 10 mW was tuned to 20 192 cm^{-1} to excite the $k = 0$ state of the lower exciton band. The linearly polarized laser field and the rf magnetic field were applied parallel to the crystal c axis. The thickness of the crystal is about 4 mm. The heterodyne beat produced at a silicon photodiode was measured as a function of the rf frequency. The phase of the beat signal relative to the rf source was corrected for the electric delay of the cables and the phase delay at the coil around the sample. The maximum intensity of the beat signal was about 10^{-4} of the dc photocurrent at the photodiode. The signal was accumulated over 1000 scans to improve the signal to noise ratio.

Figure 3 shows absorptive and dispersive components of the Raman heterodyne spectrum of the triplet exciton of 1,4-DBN at 1.5 K. The signal at 120 MHz is the z-y ESR transition. The signals at 230 and 275 MHz are the exciton NQR of ^{81}Br and ^{79}Br, respectively. NQR in the ground state does not contribute to the coherent Raman scattering [see discussion below Eq. (9)]. The ESR and NQR signals are not saturated in the rf power range from 200 μW up to 20 mW. When the rf power is increased to 200 mW, the ESR line shape changes as shown in the upper spectrum of Fig. 3. Some of the components in the inhomogeneously broadened ESR line may be saturated at this level of rf power. Different crystals from the same batch of the Bridgeman growth gave essentially the same spectrum and the rf power dependence.

The second-order susceptibility describing the coherent Raman process is proportional to the population difference between the spin sublevels and three transition matrix elements [11]. As for the Raman scattering by a magnetic transition between spin sublevels α and β in the exciton state E, the three matrix elements are of the magnetic transition and two optical transitions that connect states α and β to a spin state g in the ground state G:

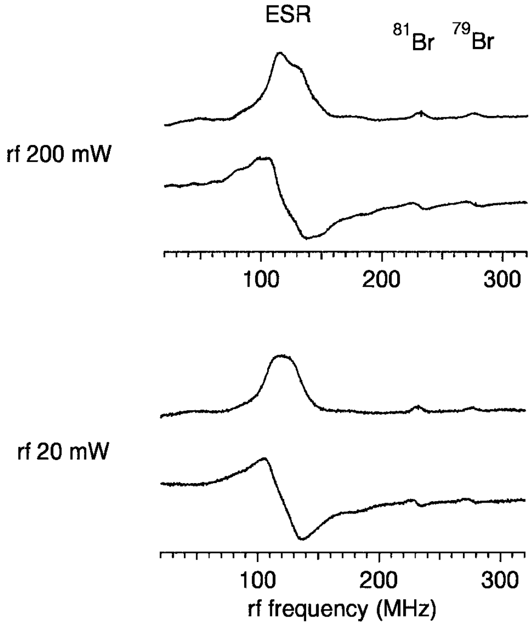

FIG. 3. Coherent Raman spectrum of the triplet exciton in 1,4-DBN at 1.5 K. The $k = 0$ state of the exciton at 20 192 cm^{-1} was excited by a cw laser with a power of about 10 mW. Two spectra were taken at different rf power levels. For each spectrum, absorptive and dispersive components are shown in the upper and the lower traces, respectively.

$$\chi^{(2)} = \sum_g \Delta n_{\alpha\beta} \langle E; \alpha | \mu_B | E; \beta \rangle \langle E; \beta | \mu_{\text{opt}} | G; g \rangle \times \langle G; g | \mu_{\text{opt}} | E; \alpha \rangle \, . \tag{1}$$

Because the inhomogeneous width of the optical transition is much broader than the spin sublevel splitting, excitons at different positions in the optical absorption line will be resonant with different sublevels of g. The coherent Raman signal is a summation over scattering pathways through all the different g. The magnetic transition operator μ_B consists of the magnetic dipole transitions of the electron spin and the nuclear spins.

$$\mu_B = \hbar \gamma_S \mathbf{B}_{\text{rf}} \mathbf{S} + \sum_i \hbar \gamma_{n_i} \mathbf{B}_{\text{rf}} \mathbf{I}_i \, . \tag{2}$$

The wave function of the exciton is approximated as a product of electronic, electron spin, and nuclear spin functions: $|E; \alpha\rangle = |E\rangle |\tau_i\rangle |a\rangle$. The triplet spin function $|\tau_i\rangle$ $(i = x, y, z)$ and the Br spin function $|a\rangle$ are the eigenfunctions of the electron spin-spin interaction and the nuclear quadrupole interaction, respectively. The electric field gradient at the Br nuclei is approximated to have cylindrical symmetry around the C-Br bond [10,12]. The

Br spin functions are quantized along the y axis so that the label a is the azimuthal quantum number: $m_y = \pm 1/2, \pm 3/2$. The ground state $|G; g\rangle$ is a product of electronic function $|G\rangle$, singlet electron spin function $|\sigma\rangle$, and Br spin function $|g\rangle$. Since the C-Br direction will not change on excitation, the ground state Br spin functions can be regarded as the same as those in the exciton state.

Singlet-triplet mixing due to the spin-orbit coupling is responsible for the optical transition to the triplet exciton. The exciton wave function has a small fraction of singlet character:

$$|E; \alpha\rangle = (|E\rangle|\tau_i\rangle + d_i|E_i\rangle|\sigma\rangle)|a\rangle, \tag{3}$$

where $|E_i\rangle$ is an electronic state which couples to the triplet sublevel i. The mixing coefficient d_i is an imaginary number, because the angular momentum operator in the spin-orbit coupling is imaginary. Using Eq. (3) the susceptibility of the Raman scattering by the z-y ESR transition is expressed as

$$\chi^{(2)}(\mathrm{ESR}) = i\hbar\gamma_S B_x \Delta n_{zy} D_{\mathrm{SO}}, \tag{4}$$

where real constant D_{SO} is given by

$$D_{\mathrm{SO}} = d_y^* \langle E_y|\mu_{\mathrm{opt}}|G\rangle\langle G|\mu_{\mathrm{opt}}|E_z\rangle d_z. \tag{5}$$

In accordance with the general consideration of the coherent Raman susceptibility [13], $\chi^{(2)}(\mathrm{ESR})$ is an imaginary number. Since the x sublevel is the least radiative, the x-y and the x-z transitions are not favorable for Raman heterodyne detection.

As for the NQR in the exciton state, if there were no hyperfine interaction, there would be no coherent Raman signal: Without the hyperfine interaction, nuclear spin function $|a\rangle$ is separable as in Eq. (3). Then, the susceptibility for the Br NQR transition between $|a\rangle$ and $|b\rangle$ will contain an overlapping factor $\langle b|g\rangle\langle g|a\rangle$, which is zero due to the orthogonality. The observation of the Br NQR Raman clearly shows that the Br spin functions are modified by the hyperfine interaction. The exciton wave function is a linear combination of the Br spin functions.

$$|E; \alpha\rangle = \sum_{i,a} c_{\alpha,ia}(|E\rangle|\tau_i\rangle + d_i|E_i\rangle|\sigma\rangle)|a\rangle. \tag{6}$$

The hyperfine interaction with the Br spins is represented by the dominant xx component [10,12].

$$\mathcal{H}_{\mathrm{hf}} = \sum_i S_x A_{xx,i} I_{x,i}. \tag{7}$$

Since $S_x|\tau_x\rangle = 0$, the hyperfine mixing occurs only in $|\tau_y\rangle$ and $|\tau_z\rangle$ states. The spin Hamiltonian for the triplet electron spin coupled with one Br spin is reduced to the following four-dimensional matrix.

$$\begin{array}{c} \tau_y, \pm\frac{3}{2} \\ \tau_z, \mp\frac{3}{2} \\ \tau_y, \mp\frac{1}{2} \\ \tau_z, \pm\frac{1}{2} \end{array} \begin{bmatrix} \epsilon + E & & & \mp\frac{\sqrt{3}}{2}A_{xx} \\ & \epsilon - E & \mp\frac{\sqrt{3}}{2}A_{xx} & \\ & \mp\frac{\sqrt{3}}{2}A_{xx} & -\epsilon + E & \pm A_{xx} \\ \mp\frac{\sqrt{3}}{2}A_{xx} & & \pm A_{xx} & -\epsilon - E \end{bmatrix}. \tag{8}$$

The z-y transition frequency $2E$ is 120 MHz. From the spectrum of Fig. 3 the quadrupole splitting $2\epsilon = e^2qQ/2$ is determined to be 275 MHz for ^{79}Br and 230 MHz for ^{81}Br. The hyperfine coupling constant A_{xx} of the triplet monomer is taken from the work on the localized triplet [12] as 60 MHz for ^{79}Br and 65 MHz for ^{81}Br [14]. When the excitation is delocalized over N molecules, the hyperfine interaction decreases by $1/N$. The hyperfine interaction in the exciton can be treated as a small perturbation.

At this stage, let us consider coherent Raman scattering by NQR in the ground state. The susceptibility for the ground state NQR between $|g\rangle$ and $|h\rangle$ is given by

$$\chi^{(2)} = \sum_\alpha \Delta n_{gh}\langle G; g|\mu_B|G; h\rangle\langle G; h|\mu_{\mathrm{opt}}|E; \alpha\rangle \times \langle E; \alpha|\mu_{\mathrm{opt}}|G; g\rangle. \tag{9}$$

Without the hyperfine interaction the susceptibility is zero, because it will contain zero overlapping factor $\langle h|a\rangle\langle a|g\rangle$. Even when the hyperfine interaction is taken into account, the ground state NQR does not contribute to the Raman signal: the population factor in the ground state Δn_{gh} can be assumed to be independent of the excited state α; substitution of Eq. (6) into Eq. (9) will result in $\chi^{(2)} = 0$ due to the orthogonality $\sum_\alpha c_{\alpha,ih}c^*_{\alpha,jg} = \delta_{ij}\delta_{hg}$.

Because of the hyperfine interaction, the NQR transition in the exciton state is no longer pure nuclear spin transition. Although the mixing of the electron spin function is small, the magnetic transition moment is carried exclusively by the electron spin. The reason is twofold: First, the magnetic moment of the electron spin is about 2500 times larger than the Br nuclei. Second, because the optical transition is a singlet-triplet transition, the electron spin contribution to the Raman susceptibility is not subject to the cancellation due to the orthogonality. The perturbation calculation using Hamiltonian of Eq. (8) leads to the following expression of the NQR Raman susceptibility for one Br spin:

$$\chi^{(2)}(\mathrm{NQR}) = i\hbar\gamma_S B_x \Delta n_{\pm 1/2, \pm 3/2} \frac{3\epsilon E/4}{(\epsilon^2 - E^2)^2} A_{xx}^2 D_{\mathrm{SO}}. \tag{10}$$

The hyperfine interaction A_{xx} is inversely proportional to the number of molecules participating in the exciton N, whereas the number of the Br nuclei involved in the exciton is proportional to N. As a result, the total NQR Raman signal scales with $1/N$. In contrast, the ESR Raman susceptibility is independent of N. Therefore, the number N can be determined by the ratio of the Raman intensity between NQR and ESR. In calculation of the ratio from Eqs. (4) and (10), the only unknown parameter is the population factor. Since the spin-lattice relaxation time is much shorter than the exciton lifetime [6,7] and the ESR and NQR Raman signals are not saturated, Boltzmann equilibrium can be assumed among the exciton spin sublevels.

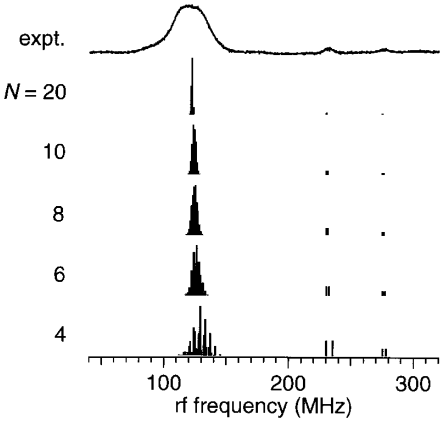

FIG. 4. Coherent Raman spectrum calculated for the exciton in 1,4-DBN delocalized over N molecules. The result is shown as histograms of the width of 1 MHz. The observation is shown on the top for the sake of comparison.

The result of the perturbation calculation is shown in Fig. 4. For the exciton delocalized over N molecules, NQR signals of the $2N$ Br nuclei were summed up with natural abundance of the two isotopes. As N decreases, the NQR intensity increases. The linewidth of ESR also increases due to the second order shift of the transition frequency. The ratio of the observed signal intensity between NQR and ESR falls in the range of the values calculated for $N = 8 \sim 13$. The linewidth, however, is better reproduced by calculations for smaller N. Distribution of the chain length and the transition frequency may contribute to the linewidth of the ESR.

The ^{13}C isotope shift of the optical transition energy is around $+2\ \mathrm{cm}^{-1}$, which is large enough to cause exciton scattering [5]. Given the natural abundance, about 11% of the molecules contain more than one ^{13}C. The exciton coherence length will be longer than the average chain length of ^{12}C isomers. Although our result of $N \approx 10$ includes additional defect scattering, it suggests that the coherence length of the exciton is limited by scattering due to ^{13}C isomers.

In conclusion, coherent Raman scattering by Br NQR and ESR of the triplet exciton of 1,4-DBN was observed. Scattering intensity of the Br NQR reflects the hyperfine interaction between the delocalized electron spin and the local Br spins. Analysis of the coherent Raman susceptibility reveals that the exciton is delocalized over about 10 molecules, which indicates scattering by ^{13}C isomers limits the coherence length of the exciton.

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