Resonant intensification of single-phonon scattering of light; excitation profiles of quasilocal modes in the KBr:MnO_4^- crystal

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The excitation spectra of that resonant Raman scattering of light by phonons of a KBr crystal which is induced by an impurity molecule MnO_4^- have been measured for the first time. The results show that low-symmetry phonon modes participate in a Jahn-Teller effect in the T_2 electronic state of the impurity.

Resonant Raman scattering of light is finding progressively broaden applications as a method for studying electronic-vibrational excitations of matter.[1] Detailed information on the parameters of the electronic-vibrational interaction in impurity molecules is embodied in the dependence of the scattering cross section σ_v of the individual vibrational modes ν_v in the spectrum of resonant Raman scattering on the excitation frequency ω_e: the excitation profiles. The dependence $\sigma_v(\omega_B)$ is determined by the resonant behavior of the components of the electron-polarizability tensor $P_{\alpha\beta}^{if_v}$ of the given vibrational transition $i \to f_v$ in accordance with the familiar Kramers-Heisenberg formula

$$\sigma_v(\omega_e) \sim \omega_e^4 \sum_{\alpha,\beta} |e_\beta P_{\alpha\beta}^{if_v} e_\alpha|^2, \quad P_{\alpha\beta}^{if_v} = \sum_m \frac{\langle f_v | M_\beta | m \rangle \langle m | M_\alpha | i \rangle}{\epsilon_m - \epsilon_i - h\omega_e + i\gamma_m}. \qquad (1)$$

Here M_α and M_β are components of the dipole-moment operator of the transitions involving the absorption of a photon (ω_e) and involving the emission of a photon ($\omega_e - \nu_v$); e_α and e_β are components of the polarization vector of the incident and scattered light; and m is the index of the electronic-vibrational excitations which have taken place. With a single absorption spectrum, a center has a set of excitation-profile spectra for vibrational modes differing in symmetry and in the number of vibrational quanta produced. It thus becomes possible to distinguish the contributions of the individual vibrations to the absorption. For a completely symmetric vibration and for an allowed dipole transition, the matrix elements of the operator M can be calculated in the Condon approximation. The excitation profiles of the fundamental, completely symmetric vibration and of its overtones contain series of resonances whose intensities are controlled by the Frank-Condon factors. The resonances in the excitation profiles for incompletely symmetric vibrations stem from the dependence of the transition matrix elements on the nuclear displacements of a given type. They also identify the vibron mixing involving the given vibration.

In the present letter we support a study of the resonant intensification of scattering involving the excitation of crystal vibrations near an impurity for the particular case of the MnO_4^- impurity molecule in a KBr crystal. We have carried out the first measurements of the excitation profiles for various regions of one-phonon scattering.

We use the results of these measurements to interpret the structure of the phonon wing in the absorption spectrum. We show that low-symmetry phonon modes are involved in a Jahn-Teller mixing. A resonant intensification of one-phonon scattering has previously been observed only for F-centers in alkali halide crystals.[2]

The KBr:MnO_4^- crystal is a convenient system for studying resonant Raman scattering by intramolecular vibrations,[3,5] including measurements of the excitation profiles of resonant Raman scattering by the completely symmetric vibration ν_1 and its overtones. The MnO_4^- molecule is excited in the dipole-allowed transition $^1T_2$–$^1A_1$, in which vibron bands of the Condon series, $\nu_{00} + n\nu_1'$, are singled out [$\nu_{00} = 18\,393\ \text{cm}^{-1}$, $\nu_1'(a_1) = 765\ \text{cm}^{-1}$]. The excitation profile for the fundamental vibration $\nu_1 = 850\ \text{cm}^{-1}$ contains resonances of a Condon series.[3–5] At a low temperature, the vibron absorption bands[6] and the excitation profiles[5] have a fine structure. Figure 1a demonstrates the correspondence between the low-frequency resonances in the zero-zero vibron band of these two spectra. The maximum at $\nu_{00} + 315\ \text{cm}^{-1}$ corresponds to the excitation of the incompletely symmetric vibration $\nu_4'(t_2)$. We observe a resonant intensification of the lines of resonant Raman scattering of molecular vibrations of t_2 symmetry, $\nu_3 = 930\ \text{cm}^{-1}$ and $\nu_4 = 409\ \text{cm}^{-1}$; this obser-

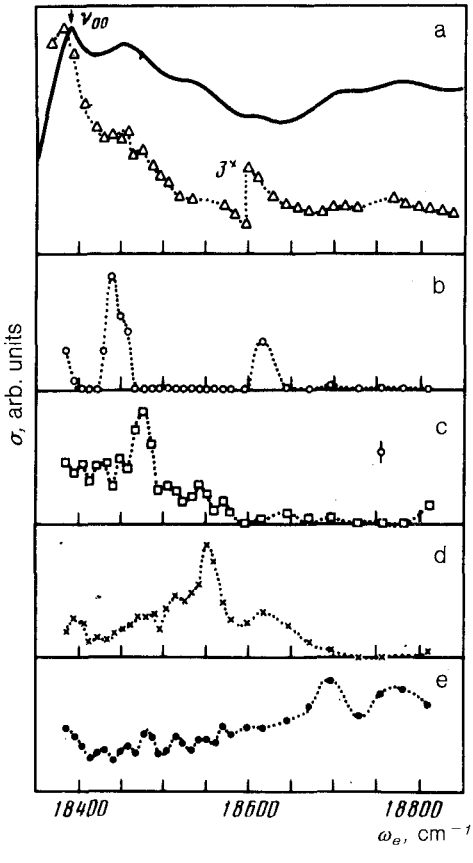

FIG. 1. Cross sections (σ) fo resonant Raman scattering by molecular and phonon modes of the KBr:MnO_4^- crystal at 5 K versus the excitation frequency ω_e. a—For the molecular vibration $\nu_1 = 850\ \text{cm}^{-1}$; b, c, d—for the regions of the phonon spectrum marked in Fig. 2; e—for the molecular vibration $\nu_4 = 409\ \text{cm}^{-1}$; solid line—the part of the absorption spectrum over which the excitation was scanned.

vation proves that these vibrations are participating in a vibron mixing of excited states of a center.[3,5] In order to interpret the transitions involving the excitation of frequencies in the region of the phonon spectrum of a crystal matrix, it is not sufficient to take phonon modes of the pure crystal of suitable frequency as additional Condon oscillators, as was done in Ref. 7. It is necessary to determine the changes caused in the phonon spectrum by the impurity molecule, to allow for the symmetry of the phonon modes, and to obtain data on the nature of the electron-phonon coupling. All these results have been obtained from the spectra of resonant Raman scattering and from the excitation profiles.

The spectrum of one-phonon scattering induced by an impurity in the KBr:MnO_4^- crystal has several structural features, including a gap mode at 92.5 cm^{-1} of symmetry t_2 and a quasilocal optical mode at 165 cm^{-1}, of symmetry a_1 or e (Ref. 5). We have observed the spectrum of one-phonon scattering in combination with the resonant-Raman-scattering line of the ν_1 vibration (Fig. 2). We have also observed a resonant intensification of one-phonon scattering upon the excitation of MnO_4^-. The degree of polarization of the ν_1 line during excitation near the 0-0 transition is 85%. The ratio of the intensity of the phonon wing to that of the line in the perpendicular polarization is an order of magnitude higher than in the parallel polarization, and there are differences in the wing structure. The depolarization of the completely sysmmetric vibration is evidence of the appearance of off-diagonal components in the scattering tensor. Such an event would be possible only upon a mixing of the wave functions of the T_2 electronic state, i.e., a Jahn-Teller effect with t_2 vibrations.[8] The phonon wing in the perpendicular polarization should apparently reflect the involvement of phonons of the local dynamics in this process. It turns out that the one-phonon spectrum of the phonon wing is very similar in structure to the one-phonon scattering spectrum of the corresponding polarization. This similarity is a consequence of the resonant nature of both spectra.

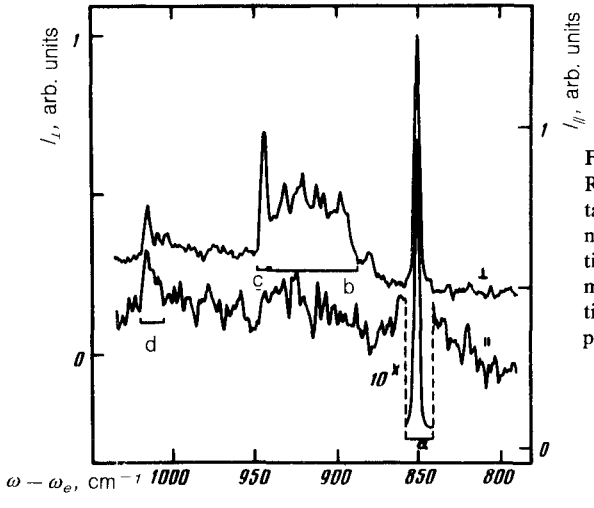

FIG. 2. Part of the spectrum of resonant Raman scattering of the KBr:MnO_4^- crystal at 5 K and of the excitation spectrum near ν_{00}, containing the line of the ν_1 vibration and its phonon wing. ||—The experimental geometry $x(zz)y$, parallel polarization; ⊥—the geometry $x(zx)y$, perpendicular polarization.

For a more detailed identification of the phonons involved in the electronic excitation, we singled out three parts of the phonon spectrum (b, c, and d in Fig. 2) which contain, respectively, a region of acoustic phonons, a gap mode in the perpendicular polarization, and an edge optical mode in the parallel polarization. We followed the intensification of these regions in the spectrum of one-phonon scattering as a function of the excitation frequency. The excitation profiles found after the necessary scaling are shown in Figs. 1b–1d. These profiles show the frequency regions in which the excitation selects given phonon states in the electronic state T_2. The resonance in the excitation profiles would correspond to maxima in the absorption if we were to ignore the interference of overlapping vibron excitations. On the basis of Fig. 1b it can be asserted that the most intense maximum in the absorption fine structure, at the frequency $\nu_{00} + 60$ cm^{-1}, is a consequence of transitions involving the excitation of acoustic phonons of t_2 symmetry. Such transitions unavoidably cause a mixing in the T_2 state. In the projected density of these phonons in the T_2 state we find a maximum at 47 cm^{-1}. Figure 1c shows that the excitation of the t_2 gap mode also occurs and is accompanied by a decrease in the frequency of this mode from 92.5 cm^{-1} in the ground state to 84 cm^{-1}. Figure 1d shows that the maximum in the absorption at $\nu_{00} + 160$ cm^{-1} is a consequence of an optical edge mode, which becomes significantly delocalized in the T_2 state, as is demonstrated by the broad range of its resonant excitation. Figure 1e proves that the $\nu_4(t_2)$ vibration is involved in the vibron mixing in the T_2 state. This result also explains the signficant decrease in its frequency (the decrease is 23%, in contrast with the 10% decrease for the ν_1 vibration).

In summary, the positions of the resonances in the excitation profiles, which fix the frequency distribution of the local dynamics around the MnO_4^- in the T_2 state, provide a basis for a complete calculation of this dynamics. Such a calculation is complicated by the involvement of phonons in the vibron mixing of the T_2 state. The polarization of the line of resonant Raman scattering of the $\nu_1(a_1)$ is 85%, giving us an estimate of the strength of the Jahn-Teller mixing, summed over all the vibrations involved. This estimate can be classified as an intermediate value. It follows from Fig. 1 that the low-frequency modes which are selected have electron-phonon couplings of comparable strengths. A quantitative interpretation of the intensities of the resonances in the excitation profiles, however, will require solving the problem of Jahn-Teller $T_2 - t_2$ mixing for MnO_4^-, with allowance for all of the low-frequency modes considered by us.

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