

Determination of multimode vibronic interaction parameters from low-temperature profiles of resonant scattering of light. Excitation of resonant scattering of light. KBr:MnO₄⁻ crystal as example

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Measurements are made of the low-temperature (5 K) polarized single-phonon scattering spectra of the Jahn-Teller MnO₄⁻ center in KBr. Also measured are the dependences of resonant Raman-scattering spectrum sections that include the lines of the molecular vibrations $\nu_1(a_1)$, $\nu_3(t_2)$, $\nu_4(t_2)$, $2\nu_4(a_1 + e + t_2)$ and of the phonon wing accompanying the ν_1 line on the excitation frequency scanned within the ${}^1T_2 \leftarrow {}^1A_1$ electron absorption band. Excitation profiles (EP) are determined for molecular and quasilocal phonon modes. A one-to-one correspondence is established between the resonances in the EP and the structure of the absorption-spectrum phonon wing. The EP for molecular and localized crystalline vibrations of the center are calculated by the absorption-spectrum transformation method. Comparison of model calculations with the EP measurements is used to determine the parameters of the vibronic interaction in the 1T_2 excited electron state.

1. INTRODUCTION

One of the most fruitful ideas of molecular spectroscopy is vibronic mixing (VM), i.e., mixing of electronic states of a molecule with not totally symmetrical vibrations, a procedure invoked to interpret electronic-vibrational transitions, excitation relaxation process, the reactivity of molecules, and others.^{1,2} For molecules introduced into crystal matrices, and also for defects of the crystal itself, the VM problem is in principle a multimode one, since account must be taken of the interaction of the electronic state of the center with the crystal vibration. A correct treatment of the latter requires in turn allowance for phonon-spectrum distortions due to interaction with the center in both the ground and the excited electronic states.

Luminescence excitation spectra and absorption spectra are traditionally used for the study of VM in impurity molecules (molecular centers). To this end, more use is being made lately of measurements of resonance Raman scattering (RRS) and of excitation profiles (EP), which describe the dependence of the cross section on the excitation frequency. Being Raman analogs of the absorption spectrum, EP yields more information.³ EP spectra measured at low temperatures (i.e., under conditions when the impurity-absorption spectrum has the structure of zero-phonon lines and phonon wings) permit a detailed study of the part played by molecular vibrations and by crystal-lattice vibrations in the VM process.⁴

We consider in this paper a method for determining the parameters of VM by analyzing low-temperature RRS and EP spectra. Using the published⁵⁻⁷ data and the results obtained in the present study for the tetrahedral impurity molecule MnO₄⁻ in a KBr crystal, we consider in detail the multimode effect of Jahn-Teller (JT) mixing of the orbital components of the electronic state 1T_2 by t_2 -symmetry molecule and crystal vibrations.

2. MANIFESTATION OF VIBRONIC INTERACTION IN RRS EXCITATION AND ABSORPTION PROFILES

The EP of RRS yield more information than the absorption spectrum because RRS is a coherent process of second

order with respect to interaction with light. In the dipole approximation the spectral distribution of electronic-vibrational absorption transitions is described by the expression

$$\kappa_\alpha(\omega) \propto \omega \left\langle \sum_m |\langle m | \hat{M}_\alpha | i \rangle|^2 \frac{\gamma_m}{(E_m - E_i - \hbar\omega)^2 + \gamma_m^2} \right\rangle_{\text{init}}, \quad (1)$$

where ω is the frequency of light, $|i\rangle$ and $|m\rangle$ are the initial and excited electronic-vibrational states with energies E_i and E_m , γ_m are the half-widths of the excited states, \hat{M}_α is a dipole-moment operator component, and $\langle \dots \rangle_{\text{init}}$ denotes temperature averaging over the initial vibrational states.

One absorption spectrum of a center corresponds to a set of RRS EP spectra for different vibrations ν_k . The dependence of the resonance contribution to the scattering cross section from the excitation frequency for a transition with creation of one vibrational quantum ν_k is determined by the Kramers-Heisenberg equation

$$\sigma_k^{\alpha\beta}(\omega) \propto \omega (\omega - 2\pi\nu_k)^3 \left\langle \left| \sum_m \frac{\langle f_k | \hat{M}_\beta | m \rangle \langle m | \hat{M}_\alpha | i \rangle}{E_m - E_i - \hbar\omega + i\gamma_m} \right|^2 \right\rangle_{\text{init}}, \quad (2)$$

where $|f_k\rangle$ is the final electronic-vibrational state.

Both the absorption spectrum and the frequency dependence of the scattering cross section for scattering via the resonance denominators reflect the energies of the excited states for which the transition matrix element $\langle m | \hat{M}_\alpha | i \rangle$ differs from zero. The frequency dependence of the scattering cross section (RSR EP) for the k th vibration picks out in addition the excited states for which the transition matrix element $\langle f_k | \hat{M}_\beta | m \rangle$ differs from zero. The polarized RSR EP spectra permit separation of oscillations with different frequencies and establish correspondence between the vibrations in the ground and excited electronic states in multimode systems.

The selective properties of the RSR EP are particularly useful in the analysis of electronic-vibrational transitions induced by vibronic interaction. In the absence of vibronic

interaction and in the Condon approximation, the absorption spectrum is formed by electronic-vibrational transitions with creation of only fully symmetric vibrations for which Stokes shifts occur. Resonant enhancement of Raman scattering of light (RSL) also takes place for these vibrations. Mixing of electronic wave functions by not fully symmetric vibrations leads to nonzero matrix elements of the transitions from the instant of the onset of these oscillations, and to the appearance of corresponding transitions in the absorption, RRS, and resonances in RRS EP.

If the vibronic mixing is not very strong, non-Condon transitions are superimposed in the absorption spectrum on more intense transitions with excitation of fully symmetric vibrations. The main advantage of the EP method over absorption is that for not totally symmetric vibrations the EP separate "in pure form" transitions induced by the interactions in which they participate.⁸ A theoretical analysis of the EP spectra as functions of the character and strength of the vibronic bonds (Herzberg-Teller and Jahn-Teller bonds, allowance for interference of many modes, etc.) is reported in Ref. 8. The JT interaction of the $T \times t$ type specifically considered in that reference and its manifestation in EP are considered in Refs. 9–11.

Figure 1 shows the results of a numerical calculation of the absorption spectra and EP for T_d centers.¹¹ They show the onset of the vibronic series of t_2 vibrations with increase of the linear JT coupling constant. For weak coupling, the EP for the t_2 vibration contains two approximately equal resonances at the ν_{00} and $\nu_{00} + \nu'(t_2)$ transitions; the resonance intensities increase in proportion to the JT coupling up to a value ≈ 0.4 , above which the proportionality is violated and resonances of higher order become noticeable. This region restricts the applicability of the so-called weak linear coupling approximation.

Allowance for the quadratic terms of the JT interaction increases first of all the probability of transitions in which an even number of t_2 vibrations are produced; all the resonances undergo shifts, since the quadratic interaction changes the energies of the vibronic levels.

The foregoing circumstances will be used below for an analysis of the absorption, RRS, and RRS EP spectra of the impurity center MnO_4^- in KBr.

3. EXCITATION PROFILES OF RESONANT SCATTERING AND ABSORPTION OF AN MnO_4^- CENTER IN KBr

The tetragonal molecular ion MnO_4^- is well known for the pronounced effects of resonance amplification of RSL.^{12–15} In the KBr crystal it replaces the Br^- anion to form a T_d symmetry center. The impurity absorption of the $\text{KBr}:\text{MnO}_4^-$ crystal shows several electronic-vibrational bands,¹⁶ among which the long-wave band at 520 nm, which is vital for the excitation of RRS, belongs to the dipole-allowed transition ${}^1T_2 \leftarrow {}^1A_1$ transition. The main vibrational structure of the band is made up of transitions, allowed in the Condon approximation, of transition from the totally symmetric breathing vibration ν_1 of the molecule.¹¹ At low temperatures one observes, besides the series of zero-phonon-line (ZPL) transitions $\nu_{00} + n\nu'_1$ and the adjacent phonon wings, also a series of $\nu_{00} + n\nu'_1 + \nu'_4$ transitions. The excitation of the not fully symmetric deformation vibration $\nu_4(t_2)$ of the molecule in an electronic transition attests to its parti-

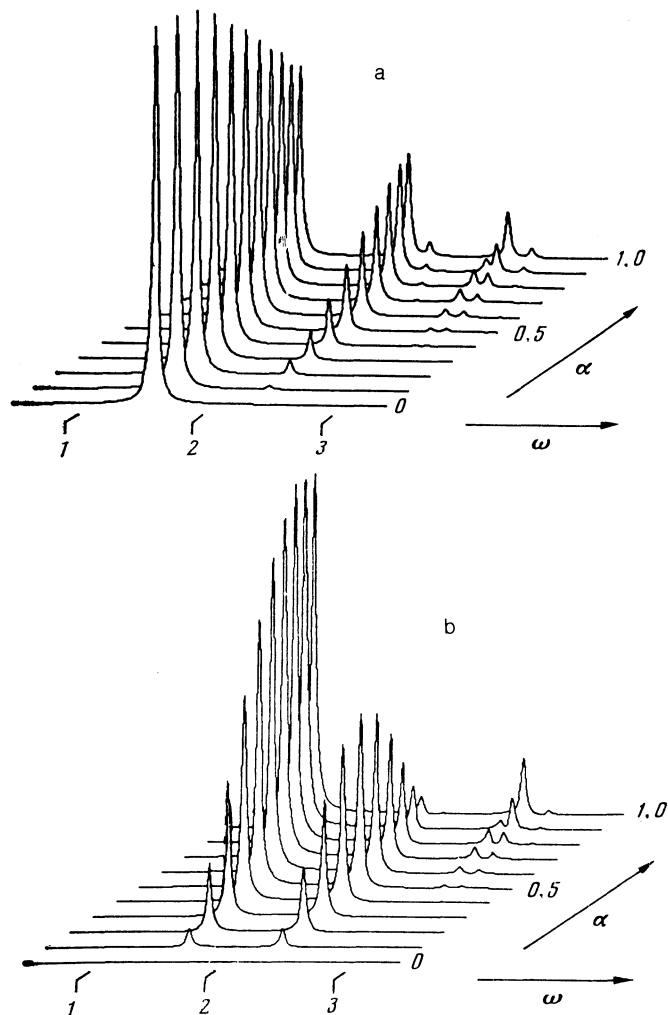


FIG. 1. Form of absorption spectrum (a) and form of RRS EP (b) for t_2 vibration vs the parameter α of linear JT interaction of an orbital triplet with a t_2 vibration.

cipation in the vibronic mixing of the 1T_2 state. The large widths of the ZPL ($\gamma_m \sim 30 \text{ cm}^{-1}$ at 5 K) are attributed to the high probabilities of the nonradiative transitions.^{5,17} A theoretical description of the spectral distribution in the absorption band, with allowance for multimode JT mixing of the components of the orbital triplet 1T_2 by t_2 -symmetry molecular and crystal vibrations, was obtained in Ref. 18, where data were used on the low-temperature RRS spectra, on the RRS excitation profiles, and on the change of the KBr crystal phonon spectrum by the MnO_4^- centers.

Let us examine these experimental data in somewhat greater detail. Excitation into the 520 nm band by individual argon-laser lines results in the vibration overtone series $\nu_1(a_1)$ typical of resonance amplification, with a nonuniform intensity distribution; it leads also to transitions with excitation of the vibrations $\nu_3(t_2)$ and $\nu_4(t_2)$ at the frequencies $n\nu_1 + \nu_3$, $n\nu_1 + \nu_4$, $\nu_3 + \nu_4$ and of the first overtones ν_3 and ν_4 (Refs. 5 and 7). At the same time, the molecular vibration ν_2 of symmetry e is not resonantly amplified. The first measurements of low-temperature (5 K) excitation profiles have shown that the ν_1 ($2\nu_1$ and $3\nu_1$) and ν_4 vibra-

tions have distinct amplification resonances that coincide with the ZPL of the pure electronic transition in absorption.⁵

A more detailed picture of the evolution of the RRS spectrum as a function of the excitation spectrum was obtained in the latest experiments in which a scanning dye laser was used and the spectrum recorded with a multichannel optical array. Figure 2 shows an unpolarized RRS spectrum section that includes the line ν_1 , the adjacent phonon wing, and also the lines ν_3 and $2\nu_4$. Scanning the excitation frequency in the absorption transition region from ν_{00} to $\nu_{00} + 2\nu_1'$ leads to resonance amplification of the intensity of line ν_1 and of its phonon wing, the latter coinciding with the ZPL ν_{00} and $\nu_{00} + \nu_1$. The amplification of lines $2\nu_4$ and ν_3 in this region is much weaker. It is interesting to track the amplification in the region of the phonon wing of line ν_1 . Besides the general amplification of the phonon wing upon excitation in the ZPL, there is observed also selective amplification of individual sections of the phonon wing upon excitation of the corresponding phonon modes in the absorption spectrum. This selectivity is manifested in the three-dimensional spectrum as amplification "furrows" which make it possible to establish a correspondence between the phonon modes in the ground and excited electronic states. The three-dimensional spectrum permits construction of excitation profiles for separate crystal vibrations localized near an impurity center.

Detailed information on the phonon spectrum of the KBr:MnO_4^- crystal was obtained with the aid of the single-

phonon scattering spectra.¹⁹ The impurity-induced polarized single-phonon scattering has revealed a substantial perturbation of the KBr phonon spectrum in the region of the acoustic and optical vibrations, including the appearance of a quasilocal symmetry mode a_1 at 165 cm^{-1} on the wing of the optical-phonon spectrum, and a gap symmetry mode t_2 at 92.5 cm^{-1} . A similar spectral structure was observed also for scattering in the region of the phonon wing of the ν_1 line. These data were used in Ref. 20 to construct a T_d -symmetry center model that includes nearest-surrounding cations and anions, to find the force constants, and calculate the symmetrized vibrational Green's function in the defective region of the crystal. The largest contribution to single-phonon scattering is made by fully symmetric shifts of the first cation sphere and by t_2 -shifts of the first anion sphere, which are responsible respectively for the edge optical and gap modes.

The first excitation profiles of phonon modes localized on the center were obtained by measuring the dependence of the single-photon scattering spectrum in the KBr:MnO_4^- crystal on the excitation frequency.⁶ Figure 3 shows the evolution of the polarized RRS spectra on a section that contains impurity-induced single-phonon scattering and the ν_4 vibration line. The spectrum of single-phonon scattering in parallel polarization shows clearly at 5 K the gap between the acoustic and optical phonons and also a quasilocal mode of frequency 165 cm^{-1} . In perpendicular polarization (Fig. 3b), which allows t_2 -symmetry, one can see clearly a quasilocal gap mode at 92.5 cm^{-1} , and also the ν_4 molecular-vibra-

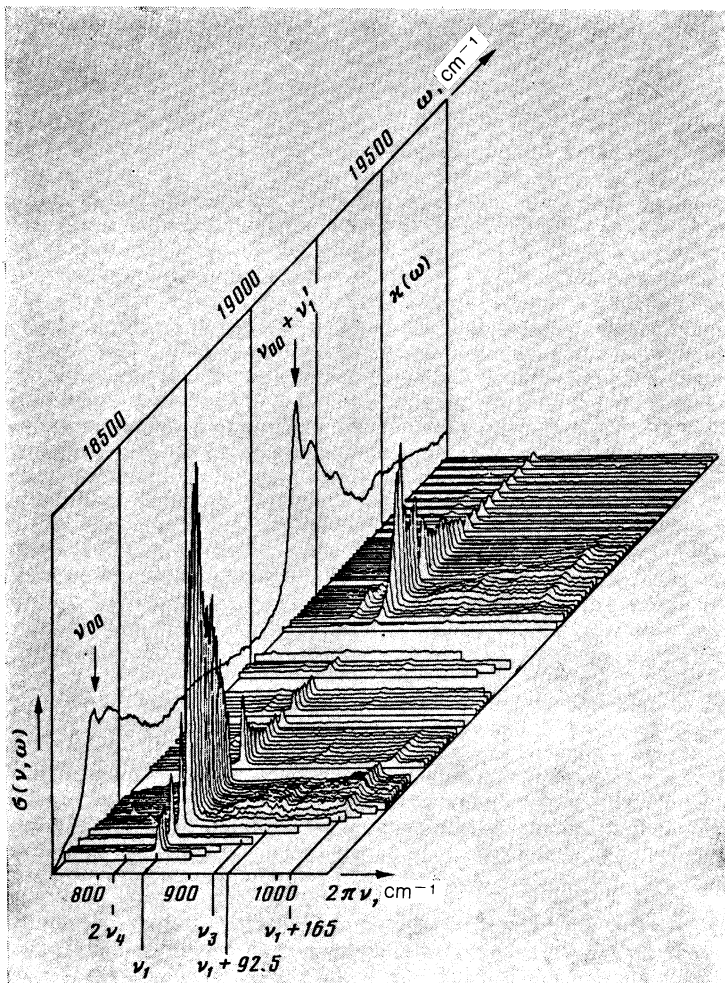


FIG. 2. Section of low-temperature (5 K) RRS spectrum of an MnO_4^- center in KBr as a function of the excitation frequency. The spectra have been corrected for absorption of the exciting light in the crystal. The vital section of the ${}^1T_2 \leftarrow {}^1A_1$ absorption band is shown.

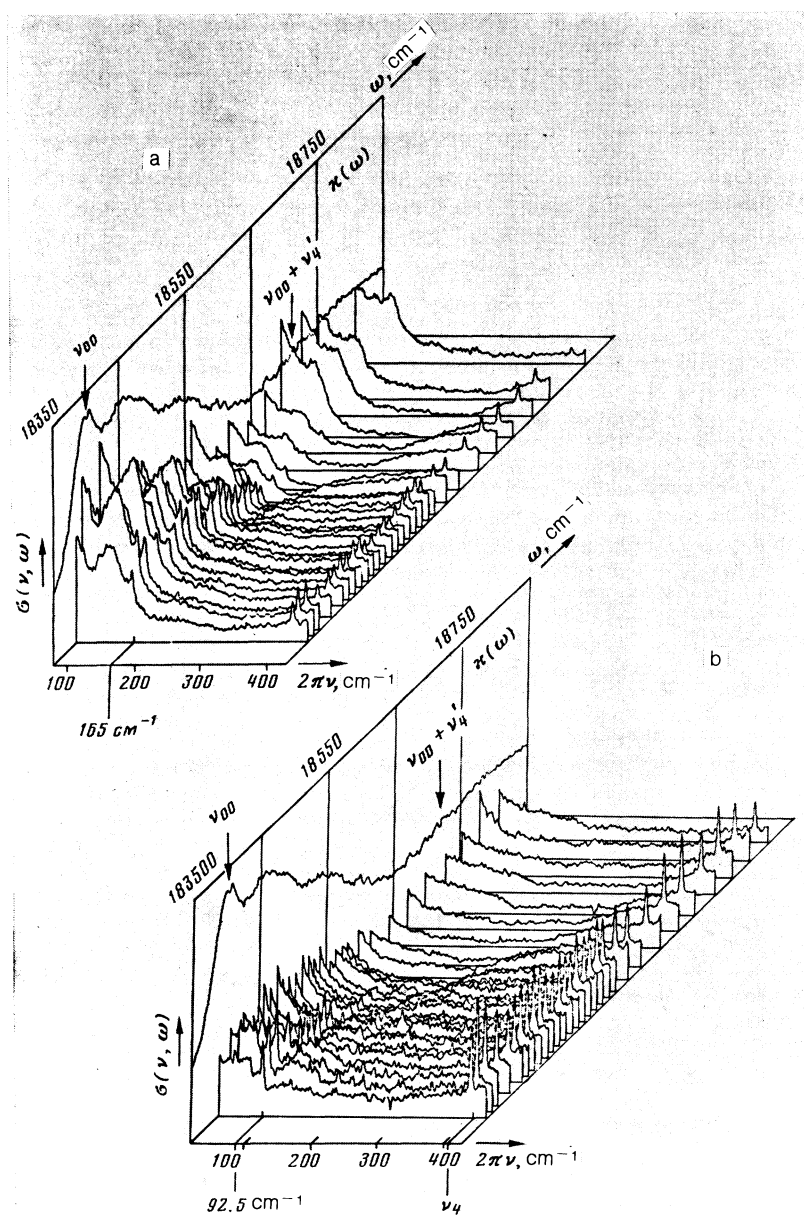


FIG. 3. Low-frequency section of polarized spectrum of RRS of an MnO_4^- center in KBr at 5 K, measured in the experimental geometries $x(zz)y$ (a) $x(zx)y$ (b). The vital section of the ${}^1T_2 \leftarrow {}^1A_1$ absorption band is shown.

tion line. Upon excitation to resonance with ν_{00} absorption ZPL, the entire single-phonon spectrum is excited, and upon excitation to the phonon wing one can clearly see the “furrows” of the selective amplification of the individual phonon modes. It can be seen that, for example, amplification of a gap mode has a distinct resonance in the absorption phonon wing at a frequency $\nu_{00} + 86 \text{ cm}^{-1}$. It is important to emphasize that the phonon-mode amplification resonances, which are narrower and more distinct than the phonon-wing peaks in absorption, establish a one-to-one correspondence between the phonon modes in the ground and excited states of the center, and thereby identify unambiguously the fine structure of the phonon wing in the absorption spectrum.

Resonance amplification of the RRS transitions with excitation of t_2 -phonons, just as their participation in the electron-phonon absorption transitions, indicates that they take part in JT mixing alongside the molecular vibration ν_4 . Figure 3a shows that for fully symmetric phonons the scattering is amplified on excitation in the $\nu_{00} + \nu_4'$ transition

region, which can also be attributed to JT mixing with the ν_4 vibration.

4. CALCULATION OF EXCITATION PROFILES AND DETERMINATION OF THE PARAMETERS OF MULTIMODE ELECTRONIC-VIBRATIONAL INTERACTION

A theoretical description of such detailed data on the excitation profiles in the RRS spectra of the MnO_4^- center in KBr calls for a solution of the problem of multimode electronic-vibrational interaction with allowance for multimode JT mixing. In this paper we determine the multimode interaction parameter by the absorption spectrum transformation method.^{21,22}

The transformation method follows from the secondary-emission theory, where the electronic-vibrational interaction in the center was considered in the time representation and using the time-correlator technique; this made possible a classification of the resonant secondary-emission components and separation of the RRS as a process that

occurs prior to the phase and energy relaxation of the optical excitation in the system.²³ The transformation method establishes the relation between the Fourier transform of the RRS amplitude and the Fourier transform of the absorption spectrum; the form of this relation depends on the model assumed for the center.

If the transitions in the center are described in the adiabatic and Condon approximation (the so-called basic model of the center²⁴), the cross section for scattering by the RRS transition with excitation of n_k quanta of fully symmetric vibration of frequency ν_k at a temperature $T = 0$, as a function of the excitation frequency ω (i.e., the excitation profile of the RRS line $n\nu_k$) is given by^{21,25,26}

$$\sigma^{0 \rightarrow n\nu_k}(\omega) \propto \omega(\omega - 2\pi n_k \nu_k)^3 \times \frac{(P_k C_k)^{n_k}}{n_k!} \left| \sum_{l=0}^{n_k} (-1)^l \binom{n_k}{l} \Phi(\omega - 2\pi l \nu_k') \right|^2 \quad (3)$$

Here $\Phi(\omega)$ is a function of the complex refractive index and its imaginary part is the reduced absorption coefficient. The $l = 0$ term in the sum is equal to $\Phi(\omega)$, the remaining terms of the alternating-sign series are calculated for the values of Φ at frequencies shifted from ω by l quanta of the given oscillation, and P_k are the dimensionless Stokes losses and play the role of a scale factor for the given EP spectrum. We have taken into account also the small frequency change in the electronic transition, by introducing the factor $C_k = 4\nu_k \nu_k' / (\nu_k + \nu_k')^2$ (Refs. 27 and 28).

For the model close to our case, that of the cubic center, where a resonance is produced with an orbital triplet and JT mixing with a not totally symmetric vibration is taken into account, the transformation method leads to expression (3) for the EP of a totally symmetric vibration and its overtones, but only so long as the weak linear JT-coupling approximation is valid.^{27,29} Within these limits, neglecting the connection with the e vibrations, the JT-coupling coefficient plays the role of a scale factor. The cross section for scattering by t_2 modes can therefore be written in the form³⁰

$$\sigma^{0 \rightarrow 1}(\omega) \propto \omega(\omega - 2\pi \nu_k)^3 \frac{\alpha_k^2}{2} C_k |\Phi(\omega) - \Phi(\omega - 2\pi \nu_k')|^2, \quad (4)$$

where α_k is the dimensionless linear JT interaction coefficient. The function $\Phi(\omega)$ of the complex refractive index was calculated in Ref. 18 from the spectral distribution in the 520 nm absorption band, using the fast-Fourier-transformation algorithm.

Equations (3) and (4) were used to calculate the RRS EP for the molecular vibration $\nu_1(a_1)$ and its first three over-

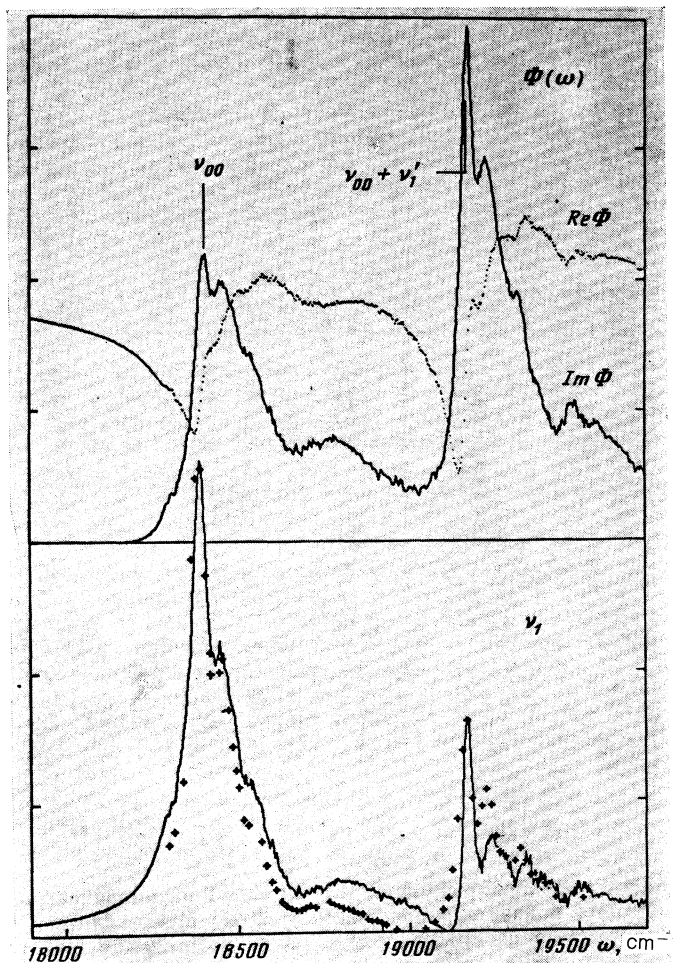


FIG. 4. Calculated EP (solid line) and EP measured at 5 K (crosses) for the molecular vibration ν_1 of an MnO_4^- center in KBr. The essential section of the function $\Phi(\omega)$ is shown.

tones, and also for the $\nu_4(t_2)$ vibration and for the gap and edge quasilocal phonon modes t_2 and a_1 at 92.5 and 165 cm^{-1} , respectively. The electronic-vibrational interaction parameters (the Stokes losses for the a_1 modes and the non-linear-JT-coupling coefficients for the t_2 modes) were determined from the condition for best agreement of the calculated and experimental EP spectra. The values obtained are gathered in Table I, which contains also the vibration frequencies in the ground and excited electronic states.

Figure 4 shows a comparison of the calculated and measured RRS EP spectra for the ν_1 vibration of the MnO_4^-

TABLE I. Parameters obtained from EP data, of the interaction of vibrations with the electronic transition ${}^1T_2 \leftarrow {}^1A_1$ in a MnO_4^- center in KBr.

Vibration	ν_k, cm^{-1}	ν_k', cm^{-1}	α_k	P_k
$\nu_1(a_1)$	850	765	—	1.71
$\nu_4(t_2)$	408	315	0.4	—
Gap mode (t_2)	92.5	9.5	0.35	—
Optical mode (a_1)	165	168	—	0.045
$1a_1$ -phonons	—	—	—	0.23
$3t_2$ -phonons	—	—	1.66	—

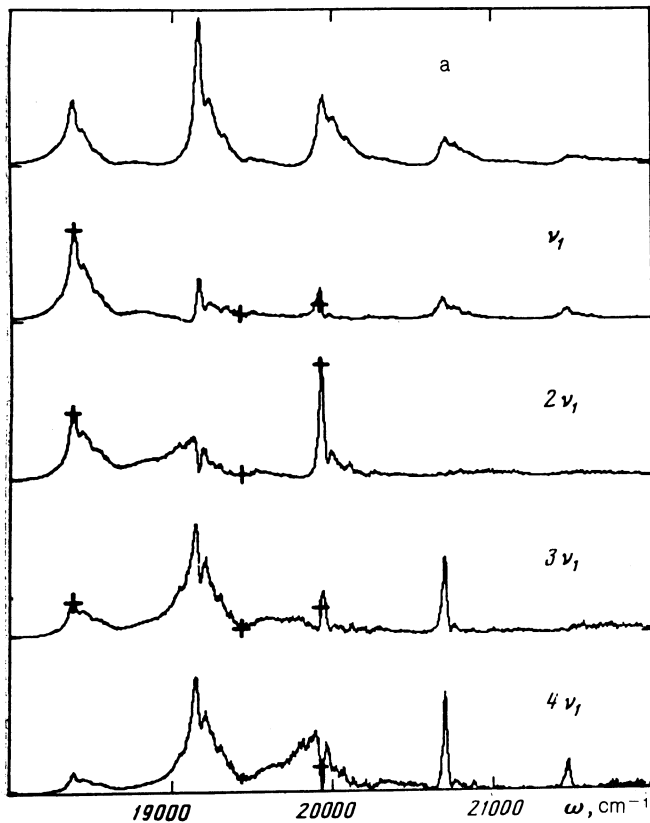


FIG. 5. Calculated EP for a Rayleigh line (a) and RRS vibration lines ν_1 , $2\nu_1$, $3\nu_1$, and $4\nu_1$ of the MnO_4^- center in KBr. The crosses mark the measured intensities of the RRS lines for the excitations at 18 400, 19 435, and 19 932 cm^{-1} according to the data of Ref. 5.

center following excitation in the absorption region from ν_{00} to $\nu_{00} + 2\nu_1'$. The experimental points were obtained from the RRS spectra of Fig. 2. The theoretical curve was calculated with a function $\Phi(\omega)$ whose essential part is shown in the upper part of Fig. 4. Recall that $\text{Im}\Phi(\omega) \propto \kappa(\omega)/\omega$.

The calculated EP for ν_1 accounts well for the resonances on transitions with excitation of molecular and crystal vibrations, both fully symmetric and of t_2 symmetry, activated by JT interaction. The appearance, in the EP calculated for ν_1 , of transitions forbidden in the Condon approximation is due to their presence in the real absorption spectrum, and hence in the function $\Phi(\omega)$. Both calculation and experiment show that the ν_1 scattering cross section vanishes near the 19 000 cm^{-1} excitation, i.e., antiresonance sets in, even though the absorption differs here from zero. Antiresonance appears in the EP because of cancellation of the difference $\Phi(\omega) - \Phi(\omega - 2\pi\nu_1')$ in the real and imaginary parts.

Figure 5 shows the EP calculated for the $n\nu_1$ lines (including the Rayleigh line) in the entire ${}^1T_2 - {}^1A_1$ absorption band. They show the irregular intensity ratio in the series and its nontrivial dependence on the excitation frequency. The calculated EP have each a number of sharp antiresonances. The $n\nu_1$ overtone intensities, measured in Ref. 5 for excitation in ν_{00} , and also by Ar^+ -laser lines, are drawn in Fig. 5 and are in fair agreement with the calculation. Thus, the low intensity of the $4\nu_1$ line for a 501.7 nm excitation corresponds to entering an antiresonance region.

We consider now the EP for the vibration ν_4 , whose resonance amplification we interpret as the result of JT mixing. The EP calculated from Eq. (4) is set in correspondence in Fig. 6 with data based on the RRS spectra of Fig. 3b. By choosing a constant JT coupling, $\alpha = 0.4$, satisfactory agreement with experiment is reached. The constant α can be determined independently of the intensity ratio of the resonances at the frequencies ν_{00} and $\nu_{00} + \nu_4'$. The experimental intensity ratio 1:0.82 yields $\alpha = 0.35$ (see Fig. 1b). Note that these values are at the borderline of the applicability of the JT-coupling weakness criterion. The obtained Stokes losses for ν_1 and the JT coupling for ν_4 describe well the RRS line intensities of these vibrations when excited in the ZPL absorption region. When excited in the phonon-wing region, the EP calculated for ν_4 is too low, possibly because of the electron-phonon coupling whose strength exceeds the smallness criterion.

Figure 6 shows also the calculated and measured EP for two quasilocal phonon modes: gap t_2 mode at 92.5 cm^{-1} and

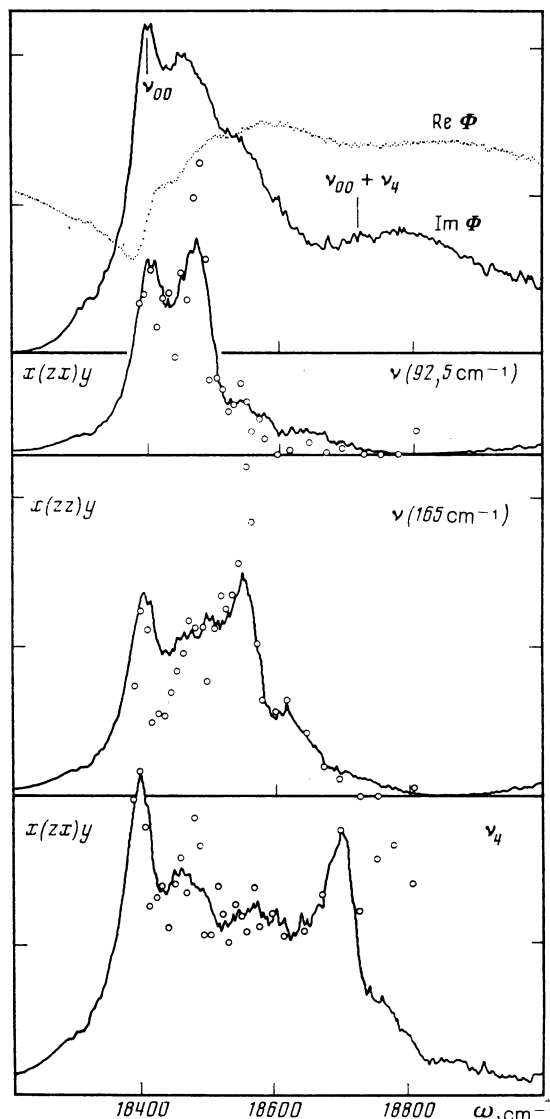


FIG. 6. Calculated RRS EP (solid lines) and those measured at 5 K (circles) for quasilocal gap and edge optical modes in the molecular vibration ν_4 of the MnO_4^- center in KBr.

edge a_1 mode at 165 cm^{-1} . In the calculation of the EP for the phonon modes, their frequencies in the excited electronic state ν'_k were chosen to obtain agreement between the measured and calculated frequencies of the second resonance. The obtained frequencies $\nu'_k = 95 \text{ cm}^{-1}$ for the gap mode and 168 cm^{-1} for the edge mode (see Table I) are close to the frequencies of these modes in the electronic ground state. This indicates that the correspondence between these vibrations in the ground and excited states is preserved (there is no Dushinskii effect), and also that the force constants binding the impurity molecule to its crystal surround is changed by an electronic transition in the center. Note that the resonance frequencies in PE on quasilocal modes are substantially shifted relative to the frequencies of the $\nu_{00} + \nu'_k$ transitions in absorption (the resonance frequencies for the gap and edge modes, 86 and 150 cm^{-1} are smaller than the corresponding ν'_k frequencies), a consequence of interference between scattering amplitudes. Interference shift occur also for EP of molecular vibrations.

The main discrepancy between theory and experiment is that the measured resonance intensities for transitions including phonon modes exceed the calculated values. One of the causes of the high intensity of the measured phonon resonances is that the JT coupling with all the t_2 -symmetry phonons is not weak. The coefficients, determined from the EP, of JT coupling with quasilocal modes (see Table I) are not large, but the smallness criterion must be satisfied for the net interaction with all the phonons connected with a given quasilocal mode.

The phonon local density of states (LDS) functions of the MnO_4^- center in KBr were calculated in Ref. 20. On the basis of the smallness of the change of the quasilocal-phonon frequencies for an electronic transition, we have used the very same functions for an approximate description of the phonon spectrum when the center goes over into the 1T_2 state. Out of the set of symmetrized LDS functions we have chosen two that have presumably the largest electron-phonon coupling, viz., LDS of symmetry $1a_1$, containing an edge optical mode, and LDS $3t_2$ containing a slit mode (see Ref. 20). The total coefficients $P(1a_1)$ and $\alpha^2(3t_2)/2$ were calculated from the relation

$$P_{(\Gamma)}/P_{\text{loc}} = \left\{ \sum_l \text{Im } G_{\Gamma}(\omega_l)/\omega_l^2 \right\} \left\{ \sum_l' \text{Im } G_{\Gamma}(\omega_l)/\omega_l^2 \right\}^{-1}, \quad (5)$$

where $G_{\Gamma}(\omega)$ is the symmetrized vibrational Green's function of the representation Γ , and the prime on the summation sign denotes summation of only the quasilocal mode.

It is useful to compare the values $P(1a_1) = 0.23$ and $\alpha^2(3t_2)/2 = 6.6$ obtained in this manner with the total Stokes losses calculated from the ratio of the area under the ZPL and its phonon wing in the absorption spectrum ($P_{\Sigma} = 1.6$). This quantity shows that the estimate of the JT coupling with $3t_2$ phonons based on the LDS is greatly overvalued. This may be a manifestation of the high sensitivity of LDS to a small change of the gap-mode frequency. As an estimate of the JT coupling with $3t_2$ phonons we chose the difference $P_{\Sigma} - P(1a_1) = 1.37$ (see Table I).

A direct verification of the proposed interpretation of electronic-vibrational transitions and of their parameters in

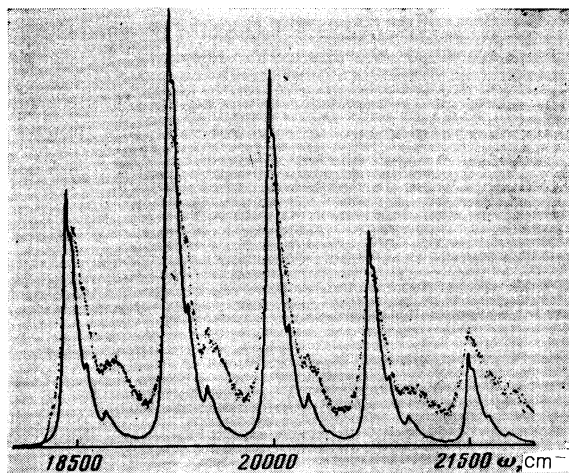


FIG. 7. Spectra of relative absorption of the MnO_4^- center in KBr, calculated with the parameters of Table I (solid line) and measured (dotted). The calculation details are given in Ref. 18.

an MnO_4^- center in KBr was made by simulating the vibrational structure of the ${}^1T_2 \leftarrow {}^1A_1$ absorption band using the parameters of Table I and the LDS functions.¹⁸ A comparison of the simulated absorption spectrum with the one measured at 5 K (Fig. 7) shows good agreement for the frequencies and intensities of all the electronic-vibrational transitions, including good agreement for the fine structure of the phonon wings. We note in particular the reproduction of the maximum of the phonon wing at the frequency $\nu_{00} + n\nu'_1 + 60 \text{ cm}^{-1}$, which is automatically obtained on account of the acoustic phonons as a function of the LDS for $3t_2$ vibrations.

We have thus verified, with the molecular center MnO_4^- in KBr as an example, a method of determining the parameters of a multimode electronic-vibrational interaction. The method is based on an analysis of a family of low-temperature EP measured for individual vibrational modes. We have shown that measurement of EP for individual quasilocal phonon modes, supplemented by an analysis of the distortions of the phonon spectrum of the matrix crystal in an impurity surrounding, makes it possible to track the variation of the LDS in an electronic transition. The method proposed is apparently the only one that permits a detailed interpretation of the participation of crystal vibrations in an electronic transition and vibronic mixing in an excited electronic state.

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¹⁾ The MnO_4^- center vibration frequencies in the electronic states 1A_1 and 1T_2 are listed in the table below.

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