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## LOW-TEMPERATURE RESONANCE RAMAN SCATTERING IN $\text{KClO}_4:\text{MnO}_4^-$

(Presented by K. K. Rebane)

### 1. Introduction

The resonance Raman scattering spectra (RRS) of a small impurity molecule in a crystal host seem to be a rather simple case suitable for a quantitative comparison with the theory [1-4]. In general accordance with the theory the RRS spectra of  $\text{I}_3^-$ ,  $\text{Se}_2^-$ ,  $\text{MnO}_4^{2-}$  and  $\text{MnO}_4^-$  molecules in alkali halide crystals [5-9] on excitations within the molecular absorption band have been observed to contain sequences of overtones of a totally symmetric molecular mode. Also the intensities of RRS lines reveal nonmonotonic irregular dependence on the scattering order and are strictly dependent on the excitation frequency. The qualitative agreement with the calculated probabilities of RRS transitions has been achieved within the frames of a simple model [10], which considers a single excited electronic state, and a scattering, concerning a single totally symmetric vibrational mode represented by a harmonic oscillator. The same mode forms a progression of vibronic bands in the absorption, which is due to the shift of the oscillator's equilibrium distance on the electronic transition. In the Condon approximation RRS line intensities are governed by the Franck-Condon principle and can be calculated easily. The best agreement with the calculations has been obtained by R. J. H. Clark and B. Stewart [11] for the  $\text{MnO}_4^-$  ion doped into  $\text{KClO}_4$ . The resonance Raman excitation profiles (REP) have been measured for the lines of  $\nu_1(A_1)$ ,  $2\nu_1$  and  $3\nu_1$ , at 300 K and found to be very close to the calculated ones throughout the entire range of the  ${}^1T_2 \leftarrow {}^1A_1$  absorption band, also taking into account the oscillator frequency shift.

The RRS and REP should be highly sensitive to electron-vibrational interactions in the molecule [12], and, therefore, the observed accordance between the experimental results and calculations based on the Franck-Condon scattering mechanism, which does not include any vibronic coupling, seems rather disappointing.

On the other hand, for  $\text{S}_2^-$  in KI the intensities of the molecular mode overtones measured at 5 K and excitation in resonance with the degenerated  ${}^2\Pi_u \leftarrow {}^2\Pi_g$  electronic transition were in a drastic disagreement with the simple model calculations [13]. The molecular absorption band of  $\text{S}_2^-$  at LHe temperature possess the structure of narrow non-phonon lines (NPL) and phonon sidebands, and on tuning the excitation frequency over the NPL we have observed a minimum (an antiresonance) in the low-temperature REP at the NPL frequency [14]. It was expected that the validity of the simple model for the totally symmetric mode of a degenerated electronic state was connected with the presence of the broad, overlapping vibronic bands in absorption.



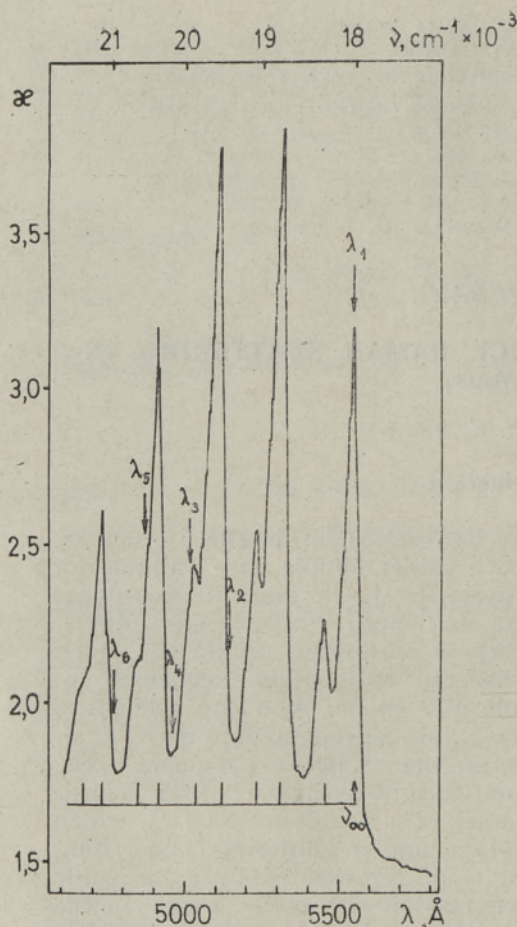


Fig. 1. Unpolarized absorption band of  ${}^1T_2 \leftarrow {}^1A_1$  transition of  $MnO_4^-$  impurity ion in the  $KClO_4$  crystal at 5 K. The arrows  $\lambda_1$  to  $\lambda_6$  represent the laser lines used for the excitations.

## 2. Experimental

Single crystals of about  $2 \times 2 \times 3$  mm<sup>3</sup> size were grown from a water solution of  $KClO_4$  with 5 mol % of  $KMnO_4$ .\*

The excitation was performed by the lines of an argon ion laser (Spectra Physics model 171) and by a dye laser on Rhodamin 110. The position of various excitations in the molecular absorption band is shown in Fig. 1. The laser beam was directed at  $\sim 30^\circ$  angle to the crystal surface and the reflected beam was recorded to control the change of the reflection coefficient on a possible crystal surface damage under excitation. To decrease the destruction of the crystal surface, the laser power (measured on the input cryostat window) was kept 60–70 mW. The spectra were recorded in the  $90^\circ$  geometry from the same crystal surface with a double spectrometer Spex 1402 with holographic gratings of  $1800\text{ mm}^{-1}$ . The signal was detected with a photon counting system and multichannel analyzer LP 4900.

\* The authors are thankful to V. Nömm for growing the crystal.



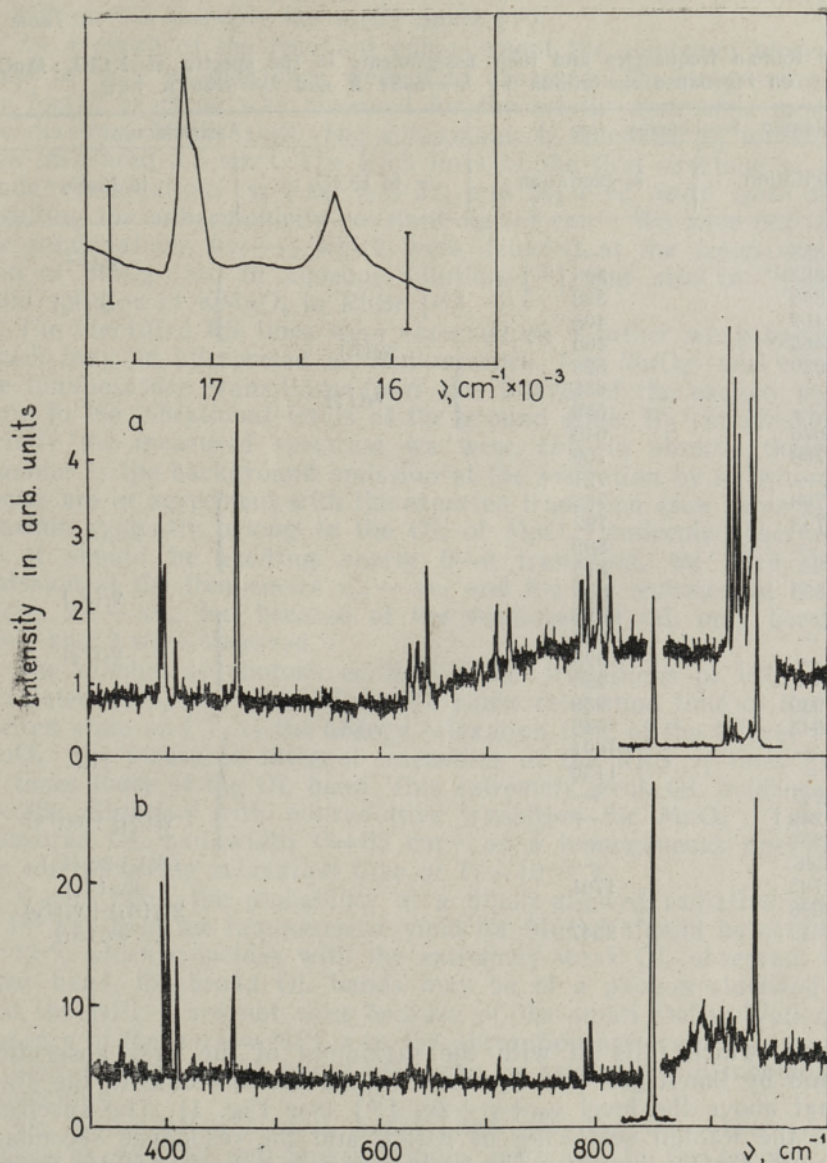


Fig. 2. A part of the first order Raman scattering spectra of  $\text{KClO}_4:\text{MnO}_4^-$  at 5 K under the excitations  $\lambda_2=5145 \text{ \AA}$  (a) and  $\lambda_1=5531 \text{ \AA}$  (b). The intensities of (a) and (b) are normalized to the intensity of the nonresonant  $\nu_1$  mode of  $\text{KClO}_4$ . The structure of a weak luminescence got by a compressing the abscissa coordinate from the spectrum (a) without Raman lines is shown in insert (the noise level is indicated).

The measured integral intensities of Raman lines on different excitations were corrected to the instrumental response and compared with the intensity of the  $\nu_1(A_1)$  fundamental of the  $\text{KClO}_4$  host crystal.

The absorption spectrum was recorded by using an Acta MVII.

### 3. Results and discussions

The full secondary emission spectrum of the crystal of  $\text{KClO}_4:\text{MnO}_4^-$  was recorded at 5 K under two excitations: by the line  $\lambda_1$  of the dye

Table 1

Measured Raman frequencies and their assignments in the spectra of  $\text{KClO}_4:\text{MnO}_4^-$  on resonance excitations by  $\lambda_1=5531 \text{ \AA}$  and  $\lambda_2=5145 \text{ \AA}$  lines

Raman frequencies (cm <sup>-1</sup> )		Assignments	
$\lambda_1$ -excitation	$\lambda_2$ -excitation	to KClO <sub>4</sub>	to MnO <sub>4</sub> <sup>-</sup>
355	—		$\nu_2(E)$
393	395		} $\nu_4(F_2)$
396	398		
407	408		
465	466	$\nu_2(E)$	
629	629	} $\nu_4(F_2)$	
—	636		
—	639		
646	646		
708	709		
—	721		
788	786		} $2\nu_4(F_2)$
793	792		
—	802		
—	813		
853	853		$\nu_1(A_1)$
—	916		} $\nu_3(F_2)$
—	922		
—	925		
—	930		
939	939	+ $\nu_1(A_1)$	
945	945		
—	1091		} HL
—	1130		
1247	—		} $\nu_1(A_1)+\nu_4(F_2)$
1249	—		
1259	—		
1646	—		$\nu_1(A_1)+2\nu_4(F_2)$
1703	1701		$2\nu_1(A_1)$
2098	—		$2\nu_1(A_1)+\nu_4(F_2)$
2549	2547		$3\nu_1(A_1)$

generation, which falls in with the maximum of the first absorption band, and by the Argon line  $\lambda_2$  which brings the molecule to the state somewhat above the level  $\nu_{00}+\nu_1+2\nu_3$  [15] (see Fig. 1). The spectrum contains the Raman scattering of  $\text{KClO}_4$  and the resonance secondary emission of  $\text{MnO}_4^-$  impurity. The parts containing the first-order Raman scattering are shown in Fig. 2, and the frequencies of all detected Raman lines are given in Table 1.

The fundamentals of infrared and Raman active crystal vibrations for  $\text{KClO}_4$  in the low-temperature phase of the symmetry  $D_{2h}^{16}(z=4)$  were discussed in [17]. According to [17], the strong line at  $945 \text{ cm}^{-1}$  pertains to the  $\nu_1(A_1)$  intramolecular stretching mode of  $\text{ClO}_4^-$  and we use it as an internal intensity standard. We observed an unsplit line at the frequency of  $\nu_2(E)$  and three crystal-field-split lines of  $\nu_4(F_2)$  mode but we observed no lines in the region of  $\nu_3(F_2)$ . One extra line near  $\nu_1$  mode at  $939 \text{ cm}^{-1}$  possibly belongs to nonequivalent groups of  $\text{ClO}_4^-$  in the crystal cell.

The lines belonging to  $\text{MnO}_4^-$  were interpreted on the basis of the available fundamental modes of  $\text{MnO}_4^-$  measured in infrared spectra of alkali halide pellets doped with  $\text{KMnO}_4$  [18]. We observed  $\nu_1(A_1)$  mode at  $853 \text{ cm}^{-1}$ , three components of the asymmetric bending mode  $\nu_4(F_2)$  at 395, 398, and  $408 \text{ cm}^{-1}$ , and three components of the asym-



metric stretching mode  $\nu_3(F_2)$  at 916, 922, and 925  $\text{cm}^{-1}$ . The weak line at 355  $\text{cm}^{-1}$  is possibly the  $\nu_2(E)$  mode [19].

As a result of the resonant enhancement the combined mode transitions as well as overtones were also observed. The progression up to the fourth overtone was observed for the totally symmetric mode  $\nu_1$  of the maximal Stokes shift. The anharmonicity constant  $x_{11}$  for this mode was measured 3.5  $\text{cm}^{-1}$ . The RRS lines of the first overtone  $\nu_4$  and the mode combinations  $\nu_1 + \nu_4$ ,  $\nu_1 + 2\nu_4$  and  $2\nu_1 + \nu_4$ , were also observed, resulting the anharmonicity constant  $x_{44}=4 \text{ cm}^{-1}$ . We have not observed the combinations  $n\nu_1 + \nu_3$  which were detected at the resonance excitation of  $\text{MnO}_4^-$  ion in aqueous solution [19] and also in  $^{18}\text{O}$ -enriched solid solution of  $\text{KMnO}_4$  in  $\text{RbBr}$  [20].

The identified RS lines were observed on a rather weak background, which may be interpreted as luminescence. For  $\text{MnO}_4^-$  one can expect the luminescence transitions from the 0-level of the excited electronic state to the vibrational levels of the ground state. By compressing artificially the measured spectrum we were able to observe three broad maxima in the background emission at the excitation by  $\lambda_1$ , whose frequencies are in agreement with the expected transition (see Table 2). These maxima evidently belong to the OL of  $\text{MnO}_4^-$  molecule observed first. As it should be exciting nearly 0—0 transition, we have the RRS emission at the frequencies  $\nu_{ex} - n\nu_1$  and the OL emission at the frequencies  $\nu_{00} - n\nu_1$ , but because of the weakness of OL only bands with  $n=1$  and 2 were observed.

The number of photons emitted in the transitions of RRS and OL is related as  $T_2 : T_1$ , where  $T_2$  is the phase relaxation time of the virtual excited state and  $T_1$  is the energy relaxation time of the 0-level [16]. For  $\text{MnO}_4^-$  the measured integral intensities of the RRS  $\nu_1$  lines exceeded 20 times those of the OL band. This extremely weak OL evidences some specific situation with nonradiative transition for  $\text{MnO}_4^-$ . Taking the measured OL bandwidth  $\Gamma=65 \text{ cm}^{-1}$  as a homogeneous one, it gives the corresponding relaxation time of  $T_1 \sim 10^{-13} \text{ s}$ .

If one takes the probability of a dipole-allowed radiative transition  $\sim 10^3 \text{ s}^{-1}$ , then the luminescence yield for  $\text{MnO}_4^-$  should be of the order of  $10^{-5}$ , which coincides with the extremely weak OL observed. On the other hand, the broad OL bands may be of a phonon sideband origin and the NPL-s are not seen because of the small Debay-Waller factor. Absence of the narrow NPL-s in the absorption spectrum may be related to their absence in OL but it may also be caused by an inhomogeneous broadening.

On  $\lambda_2$  excitation a weak background emission was observed in the Stokes as well as anti-Stokes regions from  $\nu_{00}$ . In the spectra with a compressed background, a structure was measured in the anti-Stokes region that may be interpreted as a partly reabsorbed hot luminescence: the positions of two minima at 18860 and 18080  $\text{cm}^{-1}$  coincide with

Table 2

Calculated and measured luminescence transitions for  $\text{MnO}_4^-$  ion in  $\text{KClO}_4$  at 5 K under the excitation on the maximum of 0—0 absorption band

Transitions	Calc. frequency ( $\text{cm}^{-1}$ )	Measured peak position ( $\text{cm}^{-1}$ )	Intensity (imp/s)	$\Gamma$ ( $\text{cm}^{-1}$ )
$\nu_{00} - \nu_1$	17250	{ 17150 17090	65	65
$\nu_{00} - \nu_1 - \nu_4$	16800	16780		
$\nu_{00} - 2\nu_1$	16350	16300	52	80



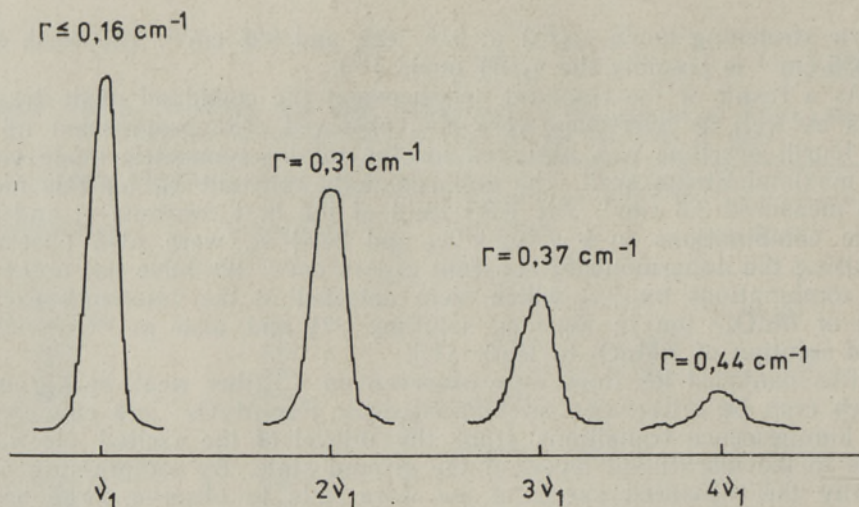


Fig. 3. Line shapes and intensities of the first four orders of RRS of  $\nu_1$  mode of  $\text{MnO}_4^-$  on the excitation in the maximum of 0—0 absorption band. The halfwidths (after correction for instrumental broadening) are indicated.

two first maxima in absorption. We also observed two prominent lines at 18305 and 18344  $\text{cm}^{-1}$  with  $\Gamma=7 \text{ cm}^{-1}$  which do not appear at  $\lambda_1$  excitation and may therefore be identified as some HL transitions.

A sequence of the four RRS lines of the totally symmetric  $\nu_1$  mode of  $\text{MnO}_4^-$  was observed at different excitations from  $\lambda_1$  to  $\lambda_6$  (see Fig. 1). The most intensive overtones were observed on the excitation by  $\lambda_1$  in the maximum of 0—0 absorption band. Fig. 3 shows the RRS line shapes and intensities measured with narrow monochromator slits of  $70\mu$  to reveal homogeneous linewidths (HLW). Fig. 3 depicts the HLW-s after the instrumental linewidth is subtracted. The anharmonic broadening of the RRS lines is clearly seen to increase with the order. For the first order  $\Gamma \leq 0.16 \text{ cm}^{-1}$  that estimates the lower limit for the anharmonic decay time  $T_1$  to be  $\geq 6 \text{ ps}$ . The increase of HLW is roughly proportional to the vibrational quantum number, as it should be for the case of an anharmonic decay of a high frequency molecular mode into crystal phonons.

The relative integral intensities of the  $\nu_1$  mode overtones measured at 5 K at different excitation frequencies are presented schematically in Fig. 4. A comparison is made to the same overtone intensities measured in [11] on the same excitations, but at the temperature of 300 K. One can see the basic difference in the intensity distribution among overtones at 5 and 300 K, and as a result, the low-temperature intensities are in disagreement with the calculated probabilities [11].

A possible quantitative understanding of the situation is based on the observed temperature dependence of the absorption spectrum. At 300 K the only resolved structure in the absorption is due to the  $\nu_1$  mode with the halfwidth of the vibronic bands being  $300 \text{ cm}^{-1}$ . With such broad overlapping bands the calculated intensities of the  $n$ -th-order resonance scattering of  $\nu_1$  mode, which take into account only the  $\nu_1$  vibrational levels, were in excellent agreement with the experiment even if the excitation frequency was falling to the minimum between two vibronic transitions in absorption. In this case the greater part of the calculated intensity is caused by the so-called interference terms.

At low temperature vibronic bands become narrower and the additional structure has appeared. In accordance with the narrowing of the



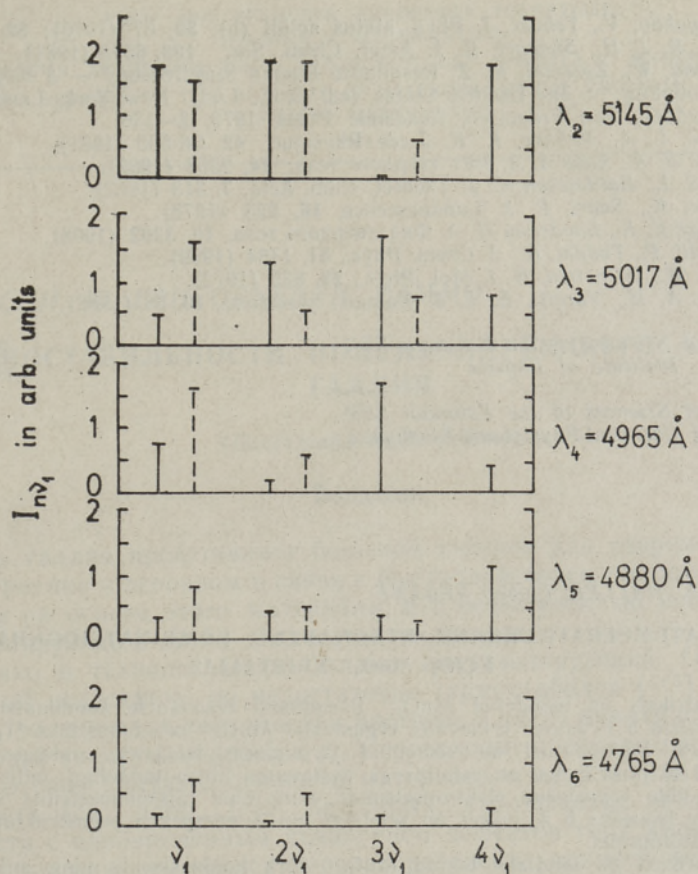


Fig. 4. Relative integral intensities of the  $\nu_1$  mode overtones at different excitation wavelengths at 5 K. Solid lines — present work, dashed lines — [11] (comparison is made by equalizing the intensities of  $2\nu_1$  mode on the  $\lambda_2$  excitation).

bands the input from the interference terms decreases and the intensities calculated in the simple model become very sensitive to the excitation frequency shift from sharp resonances in absorption. For  $\text{MnO}_4^-$  the absorption at 5 K does not reveal NPL-s, and the linewidths of the  $\nu_1$  vibronic bands on the basis of [15] are  $\Gamma \sim 60 \text{ cm}^{-1}$ . The excitations used (except  $\lambda_1$ ) are essentially shifted from the  $\nu_1$  absorption maxima and therefore cannot be described within the frames of the simple model. On excitation near the maximum (as in the case of  $\lambda_1$  excitation) the observed intensities were in accordance with the theory. The calculations taking into account the other modes are in progress.

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#### MADALATEMPERATUURILINE RESONANTNE KOMBINATSIOONHAJUMINE $\text{KClO}_4 : \text{MnO}_4^-$ KRISTALLIS

$\text{KClO}_4$  maatriksis on mõõdetud  $\text{MnO}_4^-$  lisandiooni resonantse kombinatsioonhajumise (RKH) spektrid 5 K juures erinevatel ergastustel  $\text{MnO}_4^-$  neeldumisribas  ${}^1T_2 \leftarrow {}^1A_1$ . RKH võnkekorduste intensiivsusi on võrreldud kirjanduses leiduvate andmetega, mis on saadud 300 K juures. See on rahuldavas vastavuses lihtsa mudeliga, milles on arvestatud vaid ühte ergastatud elektronseisundit ning ühte täissümmeetrilist võnkenivood. Ebarahuldav kooskõla 5 K juures on seletatav neeldumisspektri peenstruktuuriga madalatel temperatuuridel.

Esmakordselt on kindlaks tehtud  $\text{MnO}_4^-$  nõrk luminescents ning antud hinnang faasi- ja energieetilise relaksatsiooni aegadele.

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#### НИЗКОТЕМПЕРАТУРНОЕ РЕЗОНАНСНОЕ КОМБИНАЦИОННОЕ РАССЯНИЕ В КРИСТАЛЛЕ $\text{KClO}_4 : \text{MnO}_4^-$

Спектры резонансного КРС  $\text{MnO}_4^-$  в кристалле  $\text{KClO}_4$  измерены при 5 К и возбуждении в полосу примесного поглощения  ${}^1T_2 \leftarrow {}^1A_1$ . Спектр содержит вибронную серию до 4-го обертона молекулярного колебания  $\nu_1(a_1)$ , а также комбинированные частоты  $\nu_1 + \nu_4$ ,  $\nu_1 + 2\nu_4$  и  $2\nu_1 + \nu_4$ , где  $\nu_4(t_2)$  обнаруживает 3 компонента расщепления кристаллическим полем. Определены однородные ширины линий обертонов  $\nu_1$  и ангармонические постоянные. Впервые обнаружена люминесценция и горячая люминесценция иона  $\text{MnO}_4^-$ . Квантовый выход люминесценции оценен  $\sim 10^{-5}$ .