

Resonant secondary emission of Se_2^- in KI

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(Submitted 28 July 1977)

Pis'ma Zh. Eksp. Teor. Fiz. **26**, No. 10, 674–678 (20 November 1977)

Using Se_2^- in KI as an example, the complete spectrum of resonant secondary-emission is measured for the first time ever. A quantitative comparison is made with theoretical models, and the resonant-Raman-scattering and hot and ordinary luminescence components are separated. The theoretically predicted nonmonotonic distribution of the scattering cross section of the Raman-section overtones is observed.

PACS numbers: 78.50.Ec, 78.55.Fv, 78.30.Gt, 63.20.Pw

A theoretical analysis of the two-photon interaction of light with matter has shown^[1–3] that the resultant resonant secondary emission (RSE) should contain emission components that reflect various stages of the absorbed-photon conversion in the medium. The RSE spectrum was calculated for various models of an impurity center in a crystal,^[2,4] and in those cases when the model included rapid vibrational relaxation it was possible to separate in the RSE spectrum three fundamental components: ordinary luminescence (OL), which is emitted by the center after thermal equilibrium with the crystal is established, hot luminescence (HL), which is emitted from the excited vibrational levels in the course of the vibrational relaxation,^[5] and resonant Raman-scattering (RRS), which enters in the overall RSE flux.

In the present study, for the first time ever, we have registered the complete RSE spectrum separated its three fundamental components, and compared the results quantitatively with the theoretical models.

The most characteristic spectra, that admit of reliable and simple interpretation, were obtained in an impurity-center model that takes into account one isolated local vibration, whose equilibrium position and frequency vary in the electronic transition.^[4] The model takes into account the breakup of the local vibration into crystal vibrations by introducing the Lorentz width of the vibronic levels. In the adiabatic and in the Condon approximations, at a low temperature the model predicts the appearance in the RSE of two series of vibronic transitions of the local vibration^[6]: a pure electronic line and its vibronic replicas in the OL spectrum, and a Rayleigh line and its vibronic replica in the RRS spectrum. The HL spectrum is expected to consist of a superposition of series of vibronic transitions, that start with each of the vibronic levels of the excited state of the center and are populated in the course of the vibronic relaxation.

The choice of Se_2^- in the KI crystal as the “model system” of the impurity center is based on the following: first, the impurity absorption band (450–600 nm) admits of resonant laser excitation by several lines; second, the only intramolecular vibration produces a separated local vibration of the impurity center.

Figure 1 shows the RSE spectra of the KI– Se_2^- crystal at three different excitations at resonance with the $^2\Pi_u \leftarrow ^2\Pi_g$ absorption band of the impurity molecule. The OL and the RRS are distinguishable in the RSE spectrum even at first glance. The series of bands 0, 1, 2, ..., 13 adjacent to the long-wave side of the ν_{00} pure electronic transition line are the OL vibronic bands. The series of bands adjacent to the Rayleigh line are the RRS lines of different orders. The integrated intensity of the entire RRS section is $\sim 10^{-5}$ of the integrated intensity of the OL.

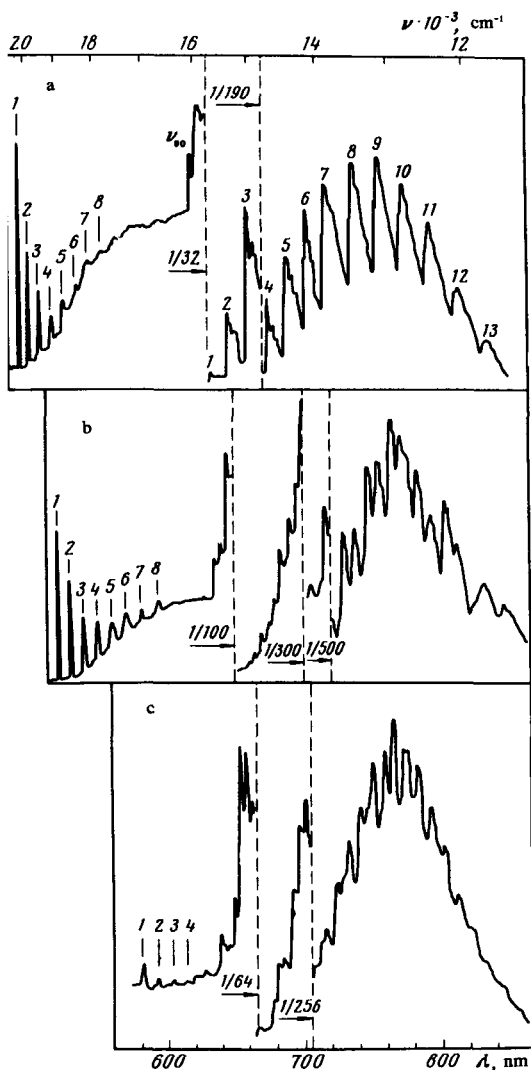


FIG. 1. RSE spectra of KI-Se_2^- crystal excited at 5 K by the following laser lines: a— $20\,486\text{ cm}^{-1}$ excitation to the 22nd vibronic level (4880 \AA line, 0.8 W); b— $19\,430\text{ cm}^{-1}$ excitation to the 16th level (5145 \AA line, 0.5 W); c— $17\,595\text{ cm}^{-1}$ excitation to the 7th level (5682 \AA line, 0.2 W).

To separate reliably the HL spectrum and to compare the measured RSE spectrum with that calculated on the basis of the model of^[4] it was necessary to specify reasonable parameters of the center; this in turn called for the construction of the adiabatic potentials of the lower electronic states.

The electronic states of the centers produced by the isoelectronic ions O_2^- , S_2^- and Se_2^- are analogous in many respects.^[6] The electronic ground state $^2\Pi_g$ is orbitally degenerate and when the molecule axis is oriented along $\langle 110 \rangle$ it splits in the crystal field into two sublevels. In the OL spectrum of the centers O_2^- and S_2^- , transitions to these two sublevels are observed as two vibronic series. In the Se_2^- spectrum one observes also a third vibronic series, whose intensity varies with the excitation frequency (cf. Figs. 1a, 1b, and 1c). The appearance of the third series was attributed to splitting of the excited electronic state $^2\Pi_u$. The three vibronic series in the OL spectrum were

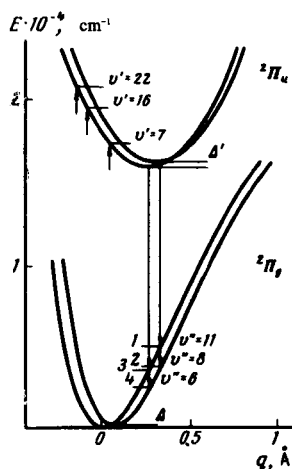


FIG. 2. Adiabatic potentials of Se_2^- center in KI. The orbital splittings Δ and Δ' of the ground and excited electronic states are equal to 220 and 152 cm^{-1} , respectively. The arrows 1, 2, 3, and 4 correspond to the maxima of the four vibronic series in the OL spectrum.

separated and the areas of the separate bands, which characterize in accordance with the Franck-Condon principle the probabilities of the individual vibronic transitions, were determined. The adiabatic potentials calculated with their aid are shown in Fig. 2. The adiabatic potentials of the electronic ground state $U_g^{(1,2)}$ were taken in the form of Morse potentials and those of the excited state $U_u^{(1,2)}$ were taken in the form of a parabola:

$$U_g^{(1)}(\text{cm}^{-1}) = 2.7 \cdot 10^4 [1 - \exp(-1.6q)]^2, \quad U_u^{(1)}(\text{cm}^{-1}) = 16040 + 2.55 \cdot 10^4 (q - 0.27)^2$$

$$U_g^{(2)}(\text{cm}^{-1}) = 220 + 2.7 \cdot 10^4 [1 - \exp(-1.6q + 0.11)]^2, \quad U_u^{(2)}(\text{cm}^{-1}) = 16192 + 2.55 \cdot 10^4 (q - 0.33)^2. \quad (1)$$

The frequencies ω_g and ω_u were obtained on the basis of the vibronic structure of the luminescence and absorption spectra.^[7] The shifts Δ and Δ' of the minima along the energy axis were obtained from the relative shifts of the vibronic series. The shift of the equilibrium position was obtained from the difference between the Stokes losses in the series (1) and (2).

The reason why the OL spectrum has three vibronic series rather than the four that follow from Fig. 2 is that the frequencies of the vibronic transitions of series (2) and (3) differ very little.

These parameters were used to calculate the RSE spectra in the HL region and the RRS region. According to^[4], the intensity of the transition $v' \rightarrow v''$ is given by the expression

$$I_{v''v'}^M \sim \frac{\xi^{2(M+v''+v')}}{M!} \sum_{h=0}^{v''} \sum_{l=0}^{v''-h} \sum_{l'=0}^{v''-h-l} (-1)^{l+l'} \times$$

$$\frac{\xi^{(-2)(2n+l+l')}}{n!l!l'!(v''-l-l'-n)!(v'-l-n)!(v'-l'-n)!},$$

where $\xi^{(2)}$ are the dimensionless Stokes losses (it is assumed that $\xi^2=11$). M determines the number of the excitation level. At $v'=M$, formula (2) yields the RRS intensity; at $0 < v' < M$ we obtain the HL transition; at $v'=0$ we obtain the OL transitions.

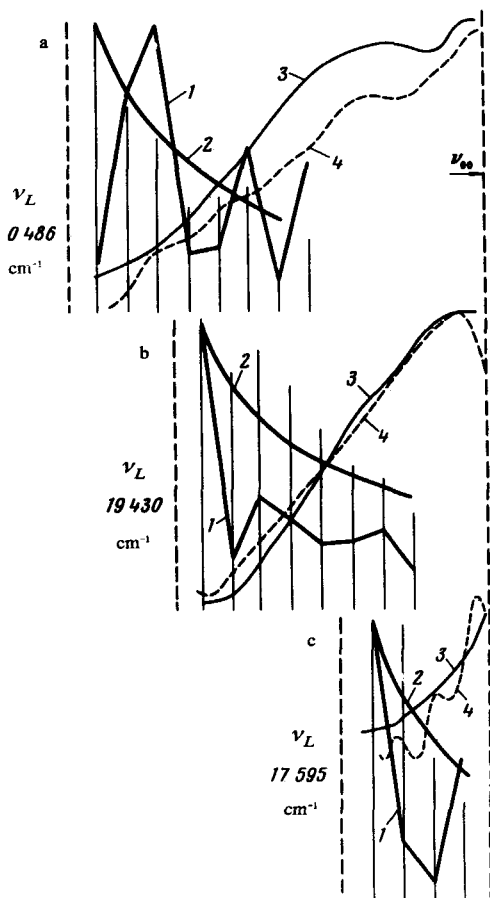


FIG. 3. Experimental and calculated RRS and HL spectra for three excitation frequencies (a, b, and c as in Fig. 1). The vertical lines correspond to the experimental values of the areas under the RRS bands on Fig. 1. Curves 1 and 2—calculation of the scattering cross sections by formula (2) and in accordance with the model of [2]. Curves 3 and 4—experimental HL spectra and those calculated by formula (2).

The broad structureless band located on Fig. 1 on the anti-Stokes side of ν_{00} was attributed to the HL in accordance with its position in the RSE spectrum. It is separated in Fig. 3 from the two other components of the spectrum. The same figure shows the results of the theoretical calculation of the HL. It is seen that the theoretical HL spectrum agrees well with the measured one. The vibronic structure in the theoretical HL spectrum is seen only for $\nu' = 7$. The absence of a distinct vibronic structure of the HL band for the excitation to $\nu' = 16$ and 22 is due to superposition of a large number of vibronic transitions, each of which has a certain width in accordance with the model.

The sharp non-monotonicity of the distribution of the scattering cross section of the RRS overtones is remarkable. In the theoretical spectrum, within the framework of the model of [4], it is the natural result of the difference between the probabilities of the vibronic transitions specified by the adiabatic potentials of the center. In accordance with the experimental data, the relative minimum of the cross sections in the RRS spectrum for $\nu' = 16$ takes place at $\nu'' = 2$. For $\nu' = 22$ calculation and experiment give relative minima at $\nu'' = 4$ and 7. Figure 3 shows also the distribution of the scattering cross sections as calculated by using for the center a model with a broad structureless electron-vibrational band. [2] It is seen that this model explains the general behavior of the dependence only in the case of excitation on the edge of the resonant-absorption band (for $\nu' = 7$).

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