

Selective excitation of the luminescence of Eu^{3+} ions in a liquid solution

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Resonant luminescence lines of impurity ions (Eu^{3+}), which differ in the composition of the solvate shell, have been selectively excited for the first time in a methanol liquid solution at $T < 200$ K.

1. The study of zero-phonon lines in the spectra of extrinsic solids yielded valuable information about various types of interactions between the impurity and the matrix (see, e.g., Ref. 1). The amount of information that can be obtained from electron-vibrational spectra was increased substantially because of the selective laser excitation which made it possible to partially eliminate nonuniform broadening.²⁻⁵

Attention has recently been drawn to the possibility for the existence of zero-phonon-line analogs in the spectra of liquid solutions.⁶ In order to see these analogs, we must first have a weak electron-vibrational interaction to insure a large Debye-Waller factor and a small line broadening at reasonably high temperatures. A nonuniform broadening in liquid solutions is dynamical in nature: The time required to change the medium surrounding the impurity may be shorter than the lifetime of the excited state, thus introducing an additional time-dependent component in the luminescence spectra. This situation was shown experimentally in the case of phthalimide molecules in viscous polar solutions by measuring the "instantaneous" spectra.⁷ Narrow zero-phonon lines have so far not been excited selectively in liquid solutions.

2. We have recently shown⁸ that the f - f line in a 5D_0 - 7F_0 transition in an Eu^{3+} impurity ion may in fact be viewed as a zero-phonon line in a liquid. In this letter we report the results of a selective laser excitation of zero-phonon lines in different impurity centers, generated by Eu^{3+} ions in alcohol solutions.

The luminescence was pumped by a cw dye laser with a 0.3-cm^{-1} line width at a power of 150 mW. The resonant emission was detected in a two-disk phosphoroscope

with a DFS-24 spectrometer at a spectral gap width of $1.5\text{--}2\text{ cm}^{-1}$. The spectra were recorded in an LP-4900 B multichannel analyzer and analyzed on a microcomputer. The test samples were $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ solutions in a perdeuterated methanol and also in acetone with a concentration of 10^{-2} M .

In organic polar solvents europium nitrate forms discrete impurity centers (solvates) which can be distinguished by the position of the ${}^5D_0\text{--}{}^7F_0$ transition line at $\sim 580\text{ nm}$ (Ref. 9). The composition of the first coordination sphere around the Eu^{3+} ion sets these centers apart from each other. The different solvates are in a thermodynamic equilibrium, which at room temperature is reached much faster than it takes an excited state to decay (τ is in the range of 0.1 to 3 ms, depending on the solvent).

3. In accordance with these arguments, at $T > 200\text{ K}$ the resonance luminescence spectrum does not depend on the length of the pump wave [Fig. 1(a)]. Upon further cooling, however, we encounter a critical temperature region in which the relaxation time of the composition of the solvate shell is comparable to the decay time of the 5D_0 state (in CD_3OD $\tau \approx 2\text{ ms}$). The selectivity of the excitation of single zero-phonon lines, which later becomes nearly complete [Fig. 1(c)], begins to manifest itself under these conditions [Fig. 1(b)]. The solution is in a totally liquid state—the melting point of methanol is 176 K; the (supercooled) solution freezes at only 160 K in the experiment. We should point out that the observed redistribution of the total intensity in favor of the short-wavelength component upon lowering the temperature stems from the thermodynamics of solvation.

The resonant nature of zero-phonon lines and the spectral selectivity are also clearly seen in the excitation spectra (Fig. 2). Here the detection in the neighborhood of 593 nm (in a broad ${}^3D_0\text{--}{}^7F_1$ band) may be assumed a nonselective detection, while the selectivity is seen in a narrow-band detection for any component of the ${}^5D_0\text{--}{}^7F_0$ transition.

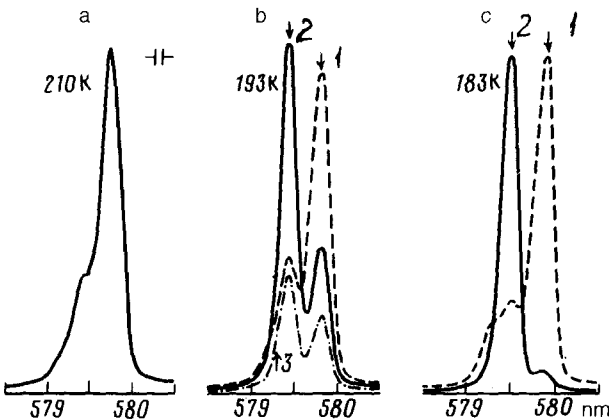


FIG. 1. Luminescence spectra of the ${}^5D_0\text{--}{}^7F_0$ transition of the Eu^{3+} ion in CD_3OD ($C = 10^{-2}\text{ M}$) in the case of monochromatic resonant excitation. (a)— $T = 210\text{ K}$, the spectrum does not depend on λ_E ; (b)—at 193 K and at the excitation wavelengths indicated by arrows: 579.85 nm (1), 579.47 nm (2), and 579.25 nm (3); (c)—at 183 K, $\lambda_E = 579.9\text{ nm}$ (1) and 579.5 nm (2), the maxima are reduced in intensity.

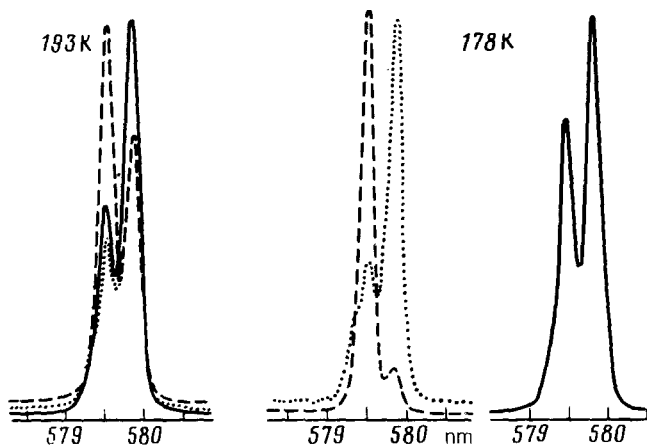


FIG. 2. Excitation spectra of Eu^{3+} in CD_3OD at 193 K (left) and at 178 K (right). Solid curve—Detection near 593 nm; dashed and dotted curves—selective detection in the short-wavelength and long-wavelength components, respectively, of the ${}^5D_0\text{--}{}^7F_0$ resonant transitions. All curves are scaled to the maximum.

Spectral selectivity is also seen in the same temperature region in other alcohol solutions (ethanol, propanol), but it is absent in acetone to the solidification point. This behavior suggests that there is a relationship between the rate at which the solvate shell is restructured and the viscosity of the solvent. As for the structure of the impurity centers studied, it has not been definitively explained, although the transition from the long-wavelength form (579.9 nm at 180 K) to the short-wavelength form (579.5 nm) can be represented as a replacement of an NO_3^- anion in the first coordination sphere by one or two water molecules in an undried solution. A smooth transition to spectral selectivity upon lowering T shows that we are in fact dealing with structurally different impurity centers in a liquid solution, rather than with centers that have been formed as a result of cooling by microcrystalline clusters. The energy barrier which divides the different discrete state of the solvate shell depends on the microscopic viscosity of the solvent. This viscosity increases rapidly upon cooling of liquids that can transform to the glassy state.¹⁰ In low-viscosity solvents (such as acetone) the relaxation of the solvate ion shell does not seem to freeze before the solidification of the solution.

In the broadening of the individual components¹⁾ the nonuniform component, which results from the differences of the more remote coordination spheres of Eu^{3+} , is the dominant component.⁸ The relaxation of these components occurs much faster (possibly in the nanosecond range^{7,11}) than in the first coordination sphere, which accounts for the absence of selectivity within single zero-phonon lines [see curves 2 and 3 in Fig. 1(b)].

We thus see that luminescence of impurity ions can be selectively excited in a liquid. This excitation can be viewed as the first evidence of a partial lifting of the nonuniform broadening of narrow zero-phonon lines in liquid solutions. Groundwork has also been laid for the direct study of the kinetics of conversion of the impurity

centers with different compositions of the coordination sphere. Initial measurements have shown that such experiments can be carried out. Structural changes of this sort are similar to a slow spectral diffusion in glasses.¹² These results raise the hope that a phonon-wing analog can also be seen in a liquid.

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¹The line width is 5 cm^{-1} at a temperature of 190 K.

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