Time-resolved spectroscopy of the zero-phonon lines in KCl:Eu2+

Larry D. Merkle and Richard C. Powell

electronically nonadiabatic scattering theory. A two-state approximation is assumed for the electronic Hamiltonian matrix $\{H_{i,j}\}$, i, $j = 2s$, $2p$, and the Demkov model assumes that the matrix elements vary with internuclear distance as

$$|H_{2s,2s} - H_{2p,2p}| = \Delta\epsilon = \text{const}$$

$$H_{2s,2p} = Ae^{-\lambda R}.$$

For large R, $\Delta\epsilon \gg Ae^{-\lambda R}$ so that the Hamiltonian is diagonal in the $2s$, $2p$ basis; for sufficiently small R, however, $\Delta\epsilon \ll Ae^{-\lambda R}$, and the Hamiltonian is diagonalized by a transformation to the states $2s \pm 2p$, i.e., $s-p$ hybrids. The change takes place in the region of R for which $|H_{2s,2s} - H_{2p,2p}| = 2|H_{2s,2p}|$, i.e., at $R = \lambda^{-1}\ln(2A/\Delta\epsilon)$.

This same type of interaction is also possible, of course, for the *triplet* interaction potential—the relevant states of helium in this case being $1s2s\,^3S$ and $1s2p\,^3P$— but asymptotically the $1s2s\,^3S$–$1s2p\,^3P$ separation is 1.14 eV, while that for $1s2s\,^1S$–$1s2p\,^1P$ is only 0.60 eV. The Demkov model thus implies that $s-p$ hybridization in the triplet case will not take place until smaller R (because $\Delta\epsilon$ is larger) where no attractive well appears because the potential is too steeply repulsive.

The Demkov picture also provides a qualitative explanation of the anisotropy of the potential inside the relative maximum (cf. Fig. 1). $s-p$ hybridization essentially places the $2s-2p$ electron on the opposite side of He from H_2, effectively bearing the $+1$ core of He to H_2. The interaction is thus qualitatively that of a charge–quadrupole, $V(R, \gamma) \sim P_2(\cos\gamma)$, so that the perpendicular geometry is most stable. (The charge–quadrupole picture is not quantitative because of the small internuclear distance.)

Calculation of the autoionization width for the singlet potential surface and cross sections for Penning ionization are in progress.

[1]M. T. Leu and P. E. Siska, J. Chem. Phys. 60, 2179, 4082 (1974).
[2]B. Brutschy, H. Haberland, H. Morgner, and K. Schmidt, Phys. Rev. Lett. 36, 1299 (1976).
[3]A. P. Hickman, A. D. Isaacson, and W. H. Miller, J. Chem. Phys. 66, 1483 (1977).
[4]J. S. Cohen and N. F. Lane, J. Chem. Phys. 66, 586 (1977).
[5]R. K. Preston and J. S. Cohen, J. Chem. Phys. 65, 1589 (1976).
[6]R. Altpeter, H. Haberland, W. Konz, P. Oesterlin, and K. Schmidt, J. Chem. Phys. (in press).
[7]The same methodology, basis set, computer programs, etc., as in Ref. 3 were used for the present calculations.
[8]C. A. Slocomb, W. H. Miller, and H. F. Schaefer, J. Chem. Phys. 55, 926 (1971).
[9]Yu. N. Demkov, Sov. Phys. JETP 18, 138 (1964).
[10]See also W. H. Miller, Adv. Chem. Phys. 25, 69 (1974).

NOTES

Time-resolved spectroscopy of the zero-phonon lines in KCl:Eu²⁺

Larry D. Merkle and Richard C. Powell

Department of Physics, Oklahoma State University, Stillwater, Oklahoma 74074
(Received 17 August 1976)

We report here the results of an investigation of energy transfer between divalent europium ions located in different sites in potassium chloride crystals. The samples used contained 275 ppm (atomic) Eu^{2+} and were excited at 3371 Å with a 5 ns pulse from a 20 kW nitrogen laser. The fluorescence at a specific time after the laser pulse was monitored with the aid of a boxcar averager.

The fluorescence spectrum of Eu^{2+} appears as a sharp zero-phonon line near 4100 Å with a broad low energy vibronic side band.[1] This is attributed to the transition from the lowest lying level of the $4f^6 5d$ configuration to the lowest component of the ground state manifold, $^8S_{7/2}(4f^7)$.[2] With high sensitivity several weak fluorescence lines can be observed in the region of the strong, sharp zero-phonon line. These are associated with zero-phonon transitions from ions in nonequivalent crystal field sites. These sites may be associated with different charge compensation since divalent europium substitutionally replaces monovalent potassium ions in KCl. The fluorescence spectra in the region of the zero-phonon lines are shown in Fig. 1 for two samples at 13 K. One sample had just been quenched to room temperature from 600 °C while the other had been slowly cooled from its growth temperature and stored at room temperature for several months. The fluorescence lifetimes of the 4095.5 and 4107.0 Å lines are 0.88 and 1.19 μs, respectively at 13 K and decreases slightly to 0.78 and 1.01 μs at 35 K. The decay curves were observed to be close to pure exponentials with rise times less than 0.1 μs. The intensity of the lower energy line increases with respect to that of the higher energy line as temperature is raised from 13 to 35 K. The ratio of the integrated fluorescence intensities plotted as a function of time after the laser pulse are shown in
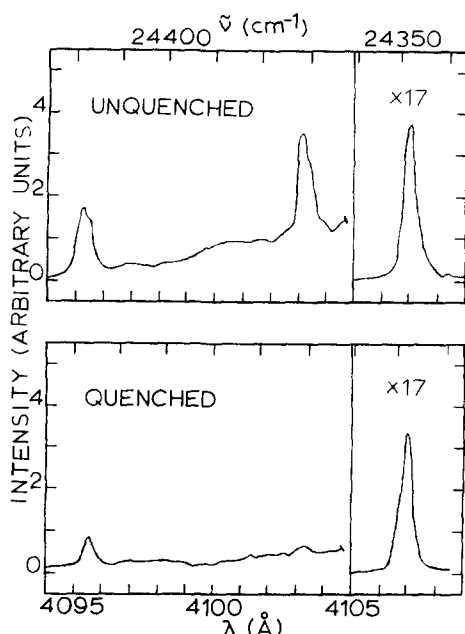
FIG. 1. Fluorescence zero-phonon lines of KCl : Eu^{2+} (275 ppm) at 13 K for quenched and unquenched samples.
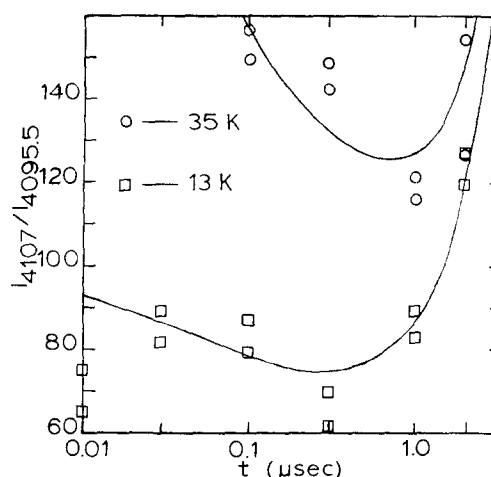

FIG. 2. Time dependences of the integrated fluorescence intensity ratios of the 4107.0 to the 4095.5 Å line at 13 and 35 K. (See text for explanation of theoretical lines.)

Fig. 2 for two temperatures. At higher temperatures the vibronic emission band is too broad and intense to allow accurate measurements to be made of the zero-phonon line parameters.

The rather complicated time dependence observed for the fluorescence intensity ratios of the zero-phonon lines can be attributed to resonant energy transfer between ions in different types of crystal field sites. Theoretical predictions for these results can be obtained from a model in which it is assumed that ions in both types of sites are directly pumped with a delta function excitation pulse and the initial fluorescence intensities are proportional to the relative numbers of ions occupying each type of site. For resonant interaction, energy transfer occurs with equal probability in both directions between ions in the two types of sites. Assuming a weak coupling, electric dipole–dipole energy transfer process, the rate equations for the populations of the excited states in the model can be solved and the solid lines in Fig. 2 represent the best fits to the data.[3]

This procedure results in a reasonably good fit to the data except for the 0.01 μs point at 13 K. The decrease in the experimental results at this time are associated with the different fluorescence rise times for the two lines which cannot be predicted by a simple direct pumping model since this is associated with radiationless relaxation from higher excited states. This simple model does, however, predict the initial decrease in the intensity ratio due to energy transfer from ions in the more populous types of sites to those in the less

populous types of sites and the subsequent increase due to the difference in fluorescence decay rates of ions in the two sites. The values of the critical energy transfer distance R_0 obtained from this fitting are 36 and 41 Å and 13 and 35 K, respectively.

A theoretical estimate for the value of R_0 can be obtained by expressing the overlap integral in terms of the width and positions of the two spectral lines assuming Lorentzian line shapes.[3] The line shapes of the two transitions were analyzed using Posener's[4] tables of Voight profiles and the Lorentzian contributions to the linewidths were determined to be about 1.5 cm^{-1} at 13 K. The oscillator strength was estimated to be on the order of 5×10^{-2} from the data of Loh,[5] the quantum efficiency was assumed to be about unity, and $n = 1.52$. These numbers give theoretically predicted values for R_0 of 30 and 34 Å and 13 and 35 K which are close to the values obtained by curve fitting. The slight increase in R_0 as the temperature is raised is due to the increase in spectral overlap caused by phonon line braodening processes.

In summary, the several zero-phonon lines in the fluorescence spectrum of divalent europium in potassium chloride are associated with ions in nonequivalent crystal field sites. Energy transfer takes place between ions in the two dominant types of sites by a resonant electric dipole–dipole interaction with a critical interaction distance of about 36 Å.

[1]K. Nasu, A. Tamura, K. Kojima, and T. Kojima, J. Phys. Soc. Jpn 36, 55 (1974).
[2]L. L. Chase, Phys. Rev. B 2, 2308 (1970).
[3]L. D. Merkle, "Energy Transfer in Europium Doped Potassium Chloride" M. S. Thesis (Oklahoma State University, 1976).
[4]D. W. Posener, Aust. J. Phys. 12, 184 (1959).
[5]E. Loh, Phys. Rev. 147, 332 (1966).