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Theoretical Spectra of Luminescent Solids

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From the potential energy curves for the ground and excited states of the thallium activator in potassium chloride, the absorption spectrum of this phosphor is calculated by direct evaluation of the matrix elements for electronic transitions between the individual vibrational levels of the initial and final states. Harmonic oscillator wave functions in the initial state and wave functions for a linear potential in the final state are used. The results verify the classical and semiclassical spectra previously reported, and provide a new insight into the application of the Franck-Condon principle to solid-state luminescence.

I. INTRODUCTION

IN a recent publication,[1] a fundamental calculation of the absorption and emission spectra of potassium chloride activated with thallium has been reported. The calculation yields the potential energy curves shown in Fig. 1 for the unexcited and excited Tl^+. The abscissa is the configurational coordinate of the system and is taken as the distance between the Tl^+ ion and its nearest Cl^- neighbors. The energies are calculated with the condition that the remainder of the lattice assumes the configuration of minimum potential energy for each value of the configurational coordinate. The curves are accurately parabolic, and the classical formula for absorption or emission spectrum can be written:

$$P(\epsilon)=(K/2\pi kT)^{\frac{1}{2}}\exp(-Kq^2/2kT)(dq/d\epsilon), \tag{1}$$

where q measures the displacement in coordinate a from the minimum for the initial state, ϵ is the difference between the two potential energy curves at q, and K is the force constant for the initial state. According to the Franck-Condon principle ϵ is the energy absorbed or emitted in the transition. In Eq. (1) the exponential measures the probability of the system having a displacement q in the initial state and the final factor is a Jacobian to take account of the change of variable from q to ϵ. The spectra computed at 80°K and 298°K by Eq. (1) were found to be in satisfactory agreement with experiment.

II. SEMICLASSICAL CALCULATION OF SPECTRA

The spectrum (1) will be in serious error at low temperatures where only a few vibrational levels* of the initial state are occupied. In particular at $T=0$, Eq. (1) narrows to a sharp line, whereas the quantum mechanical zero-point energy will insure a finite breadth. In a subsequent note,[2] therefore, the classical distribution in the initial state was replaced by the quantum-mechanical sum over the vibrational levels:

$$\rho(q)=\sum_i[\psi_i(q)]^2e^{-(2i+1)\theta/T}, \tag{2}$$

where $k\theta=h\nu/2$ is the zero-point energy, and $\psi_i(q)$ is the normalized wave function for the harmonic oscillator in the ith vibrational level at the displacement q and can be expressed in terms of the polynomial proposed by Hermite.[3] To obtain the semiclassical spectrum the exponential factor of (1) is replaced by (2), and a suitable change made in the normalization constant. Owing to the properties of the Slater sum (2) for the harmonic

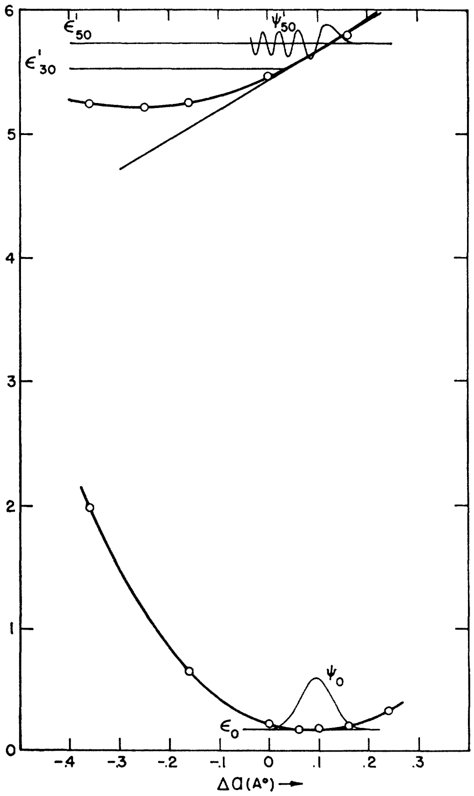

FIG. 1. Potential energy *versus* configuration coordinate plot including representative vibrational wave functions for the thallium-activated potassium chloride phosphor.

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[1] F. E. Williams, J. Chem. Phys. **19**, 457 (1951).

* *Note added in proof:*—The harmonic oscillator model follows from the assumption that the normal modes of motion which involve appreciable changes in the potential energy of the activator system are approximated by an Einstein distribution of frequency $2k\theta/h$.

[2] F. E. Williams, Phys. Rev. **82**, 281 (1951).

[3] Eyring, Walter, and Kimball, *Quantum Chemistry* (John Wiley and Sons, Inc., New York, 1944), p. 75.

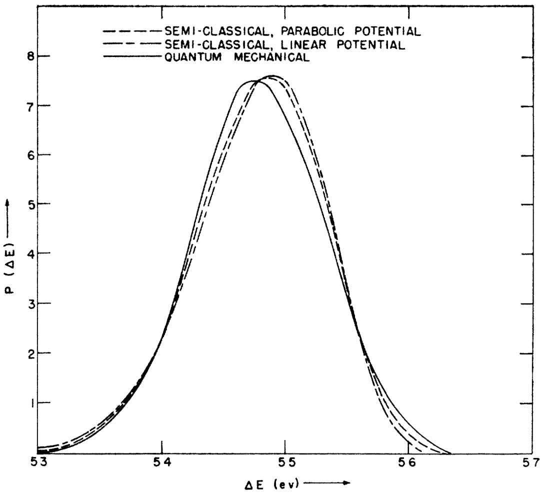

FIG. 2. Theoretical absorption spectrum of thallium-activated potassium chloride.

oscillator[4] this change is equivalent to replacing T in Eq. (1) by an effective temperature:

$$T_{\mathrm{eff}} = \theta \coth(\theta/T).$$

One notes that T_{eff} is always greater than T, approaches T for large T, and becomes equal to θ at $T=0$. For the ground state $\theta=96$°K; for the excited state $\theta=60$°K. Experimental confirmation of the theoretical absorption spectra at 4°K, 80°K, and 298°K computed semiclassically[2] have been reported.[5] The calculated absorption spectrum at 0°K is shown on Fig. 2.

III. CALCULATION OF TRANSITION PROBABILITY

The principal task of this paper is to calculate the spectra quantum mechanically. Thus, to evaluate either the absorption or emission spectrum the probability of transition between individual vibrational levels of the initial and final states must be computed. With the simplified model based on a single configurational coordinate the spectrum will consist of a series of closely spaced sharp lines. In reality other neglected coordinates will cause the lines to broaden and overlap. In the present case where no structure is observed, the theoretical spectrum will be smoothed into a continuum. The spectrum can be written:

$$P(\epsilon_{if}) = C\left[\int \psi_i \psi_f dq\right]^2 e^{-(2i+1)\theta/T}, \tag{3}$$

where $P(\epsilon_{if})$ is the probability of absorbing or emitting the energy ϵ_{if} corresponding to the transition from the vibrational level i of the initial state to the level f of the final state. The functions ψ_i and ψ_f are the vibrational wave functions for the initial and final levels. The dependence of the transition probability on the electronic wave functions and on the operator for the electronic transition is the same irrespective of the vibrational quantum numbers i and f and is included in the constant C. The exponential of Eq. (3) weights the spectrum according to the occupation probability of the vibrational levels of the initial state.

A serious problem arises in the evaluation of Eq. (3) because transitions occur to high vibrational levels in the final state. In fact, the most probable final levels are $f=41$ for absorption and $f=67$ for emission. Hermite polynomials of this order are not available in tabulated form and their computation would involve enormous labor. Therefore, a different approach is used: For evaluating Eq. (3) it is sufficient to know ψ_f in the region of configuration where ψ_i is appreciable. This region is clearly near the equilibrium configuration for the initial state since the kinetic energy of the initial state is always small. The parabolic potential energy function for the final state is, therefore, replaced by a linear potential tangent to the parabola at the equilibrium configuration for the initial state. The linear potential for absorption is shown on Fig. 1, and it is evident that the deviation from the parabola is small for a considerable range of a about $q=0$.

As a check on the validity of replacing the parabolic by the linear potential for the final state, the absorption spectrum at $T=0$°K was computed semiclassically using the linear potential. Incidentally, the semiclassical calculation in general is equivalent to substituting δ functions having nonzero values at the classical turning point for ψ_f in Eq. (3). Inspection of Fig. 2 reveals only a small difference in the semiclassical spectrum between the parabola and the tangent.

It is warranted, therefore, to evaluate ψ_f in Eq. (3) as wave functions corresponding to a linear potential. Stokes' equation must be satisfied:

$$d^2\psi/dx^2 = x\psi, \quad \text{with} \quad x = q_1(2MF/\hbar^2)^{\frac{1}{3}}, \tag{4}$$

where q_1 is the displacement in the final state measured from the intersection of the linear potential and the vibrational energy level, M is the effective mass of the oscillator, and F is the slope of the linear potential. Solutions to Eq. (4) have been tabulated in convenient form.[6] A typical vibrational wave function ψ_{50} for the excited state is shown in Fig. 1. The absorption spectrum according to Eq. (3) was computed numerically at $T=0$. The result plotted on Fig. 2 is in excellent agreement with the semiclassical spectrum. It is concluded that the spectra obtained previously by the

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[4] G. E. Uhlenbeck and L. S. Ornstein, Phys. Rev. **36**, 823 (1930), Note II; see also K. Husimi, Proc. Phys.-Math. Soc. Japan **22**, 264 (1940).

[5] P. D. Johnson and F. J. Studer, Phys. Rev. **82**, 976 (1951).

[6] "Tables of the modified Hankel functions of order one-third and of their derivatives" (Harvard University Press, Cambridge, 1945). The required solution to Eq. (4) which approaches zero for large positive x is, apart from normalization:

$$\psi(x) = \sqrt{3}R[h_1(-x)] - I[h_1(-x)]$$

in the notation of this reference. This function, with reversed sign, is plotted there on p. XXIII.

classical[1] and semiclassical[2] methods would be only slightly altered by the strictly quantum mechanical treatment according to Eq. (3).

IV. FRANCK-CONDON PRINCIPLE

The direct evaluation of the matrix elements for transitions between individual vibrational levels of the initial and final states provides new insight into the Franck-Condon principle. For absorption at $T=0$, one expects the most probable transitions to occur to levels in the excited state with vibrational quantum numbers near $f=41$, for which the classical turning point is at the equilibrium configuration for the ground state. It is clear from Fig. 1 that the probability of transition to levels with f much less than 41 will be small because ψ_i will overlap the exponential tail of ψ_f. On the other hand for f much greater than 41 ψ_i overlaps the periodic portion of ψ_f whose amplitude varies slowly; consequently, the probability of transition given by Eq. (3) will again be small because of effective cancellation arising from the rapid oscillations of ψ_f. In other words, the principal contribution to Eq. (3) results from configurations for the vibrational levels of the final state where the kinetic energy is comparable with the kinetic energy of the vibrational levels of the initial state. This is in accord with the Franck-Condon principle which states that the most probable electronic transitions leave momentum as well as position unchanged.

V. ACKNOWLEDGMENT

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Nuclear Interactions of Cosmic Rays in a Silver Chloride Crystal*

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A disk of silver chloride, cut from a large crystal grown by slowly cooling the melt, was operated as an ionization detector at sea level and at Climax, Colorado, elevation 11,200 feet. Calibration was achieved by testing the response of the crystal to single cosmic-ray particles ionizing near minimum. By means of a Geiger counter coincidence system stars produced in the crystal by ionizing particles (protons) were separated from those produced by non-ionizing particles. A pulse-height distribution is plotted for the larger pulses and is in approximate agreement with star data from photographic emulsions for energy releases in the crystal of greater than 80 Mev. Electron showers and slow protons which stop in the crystal are shown to contribute to the rates below this energy. An apparent absorption thickness in air of 114±5 g/cm^2 is obtained for the ionizing star-producing radiation between Climax and sea level. By assuming a geometrical cross section for interaction in the crystal, the intensity of energetic protons at Climax is estimated to be approximately 10 percent of the hard component.

I. INTRODUCTION

ARGUMENTS, such as those given by Rossi,[1] make it reasonable to assume that most nuclear disintegrations (stars) in the atmosphere are produced by the neutrons and protons in the cosmic radiation. The rate of star production has been shown to decrease approximately exponentially with depth in the lower atmosphere, and various observers have given absorption thicknesses for the star producing radiation from 125 to 150 g/cm^2.[2-7] A majority of low energy nuclear events (small stars) observed in photographic emulsions at moderate elevations is produced by non-ionizing radiation, that is, by neutrons. On the other hand, high energy nuclear events (larger stars containing thin prongs) vary somewhat more rapidly with atmospheric depth.[1,6,7] It is probably correct to identify these with penetrating showers. Such stars are more often produced by protons.[6] Direct information on the intensity and altitude variation of the nuclear interactions of protons is not very extensive. It should be noted that star production by pi-mesons may become important under rather thick layers of dense material.

In this paper are presented the results of a counting experiment designed to determine the rate of production of stars in a crystal of silver chloride by ionizing particles. A pulse-height distribution is given for the various events produced in the crystal. By making appropriate correlation assumptions, the distribution is compared with the star data from photographic emulsions.[6,8]

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[1] B. Rossi, Revs. Modern Phys. **20**, 537 (1948).

[2] E. P. George, Nature **162**, 333 (1948).

[3] Bernardini, Cortini, and Manfredini, Phys. Rev. **76**, 1792 (1949).

[4] N. H. Forester, Phys. Rev. **78**, 247 (1950).

[5] Lord, Schein, and Vidale, Phys. Rev. **76**, 171 (1949).

[6] Camerini, Coor, Davis, Fowler, Lock, Muirhead, and Tobin, Phil. Mag. **40**, 1073 (1949).

[7] See also the results of Bridge, Rossi, and Williams using thin-walled ionization chambers as reported in reference 1 and John Tinlot, Phys. Rev. **73**, 1476 (1948); Phys. Rev. **74**, 1197 (1948).

[8] Brown, Camerini, Fowler, Heitler, King, and Powell, Phil. Mag. **40**, 862 (1949).