

## Semiclassical Theory of the Near-Infrared Spectrum of $\text{KCl}:\text{Tl}^{0\dagger}$

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The splitting of the  ${}^2P_{3/2}$  term of  $\text{Tl}^0$  in  $\text{KCl}$  is discussed semiquantitatively in terms of a configuration coordinate representing an odd-parity vibrational mode. The gross features of the data of Delbecq, Ghosh, and Yuster (preceding paper), and in particular the temperature dependence of the splitting of the term, may be understood on this model. It is proposed that this  $T$ -dependent splitting may occur rather generally and independently of any explicit dynamical Jahn-Teller effect in forbidden transitions at impurity centers.

### I. INTRODUCTION

IN an accompanying paper,<sup>1</sup> Delbecq, Ghosh, and Yuster report an absorption spectrum associated with atomic  $\text{Tl}$  in  $\text{KCl}$  crystals (Fig. 1). This system appears to exhibit a dynamical Jahn-Teller effect in its excited states,<sup>2</sup> having a striking temperature dependence in all its characteristics (oscillator strengths, splitting, widths, and structure). The purpose of the present note is to discuss the gross aspects of the data on a very simple configuration-coordinate model which, we believe, aids in the physical understanding of the system and may have general applicability. The model emphasizes the important role of odd-parity modes, which make possible the transitions in question and also yield a  $T$ -dependent splitting of the absorption bands.

### II. A SINGLE-COORDINATE MODEL

The ground electronic configuration of  $\text{Tl}^0$  is  $6s^26p$ , and in the free atom the  ${}^2P_{3/2}$  term lies 0.97 eV higher than the  ${}^2P_{1/2}$  term. This energy difference is very close to the absorption energies observed by Delbecq, Ghosh, and Yuster, so we assume with them that the relevant ground and excited states of  $\text{KCl}:\text{Tl}^0$  are derived directly from the atomic states. Let us now assume further that the  $\text{Tl}^0$  is situated at a cubic site, that we may consider separately one vibrational mode inter-

acting with the center, and that the energies of the free atom depend on the associated configuration coordinate as illustrated in Figs. 2(a), 2(b), or 2(c). The  ${}^2P_{1/2}$  curve is simply  $\frac{1}{2}K_e Q^2$ , but the  ${}^2P_{3/2}$  curve is taken to split, according to

$$E_{1\pm}(Q) = E_0 \pm (\frac{1}{2}\Delta_0 + J_e Q + \frac{1}{2}K_e Q^2). \quad (1)$$

Figure 2(a) illustrates a "pure linear" splitting ( $\Delta_0 = K_e = 0$ ), 2(b) illustrates a "pure parabolic" splitting ( $\Delta_0 = J_e = 0$ ), and 2(c) illustrates a mixed case (only  $J_e = 0$ ). The choice among these cases is dictated by the detailed physics of the problem, as discussed below. For the moment, we fix our attention on the fact that  $E({}^2P_{3/2})$  is split in some way as a function of  $Q$ .

For the remainder of this section, let us concentrate on Fig. 2(a). As the configuration coordinate model is usually applied, vertical (Franck-Condon) transitions might take place between the lower curve and each of the upper curves. The probability distribution in the electronic ground state goes as<sup>3</sup>

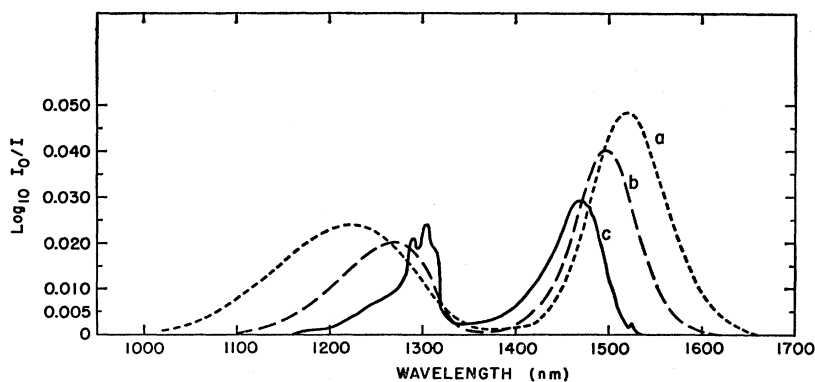
$$C e^{-\alpha(T)^2 Q^2}, \quad (2)$$

where

$$\alpha(T)^2 = (M\omega/\hbar) [\coth(\hbar\omega/2k_B T)]^{-1}. \quad (3)$$

Here  $M$  is the mass of the effective harmonic oscillator to which the ground-state curve corresponds, and  $\omega$  is its frequency. This Gaussian is shown as curve A in Fig.

FIG. 1. Absorption coefficient of  $\text{KCl}:\text{Tl}^0$  in the region 0.7–1.2 eV (after Delbecq, Ghosh, and Yuster, Ref. 1). Curves a, b, and c represent data taken at 153, 77, and 5°K, respectively.



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<sup>1</sup> C. J. Delbecq, A. K. Ghosh, and P. H. Yuster, preceding paper, Phys. Rev. **154**, 797 (1967).

<sup>2</sup> M. Cohen, as quoted in Ref. 1.

<sup>3</sup> See M. Lax, J. Chem. Phys. **20**, 1752 (1952). We have specialized the appropriate expression for the case of a single mode.

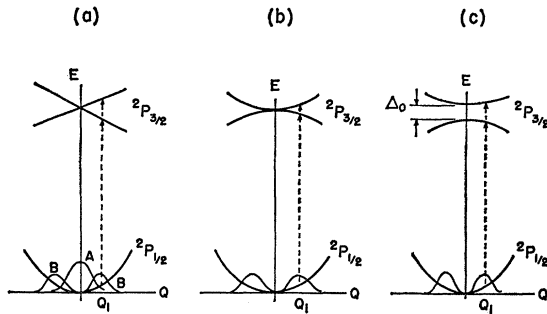


FIG. 2. Possible dependence of the energy of the system on an odd-parity normal-mode coordinate  $Q$ . Transitions take place with the greatest probability when  $Q = \pm Q_1$ , rather than at the origin, in which case there are two available excited levels. The different cases (a), (b), and (c) are discussed in the text.

2(a). If the electronic transition is allowed and its rate is independent of  $Q$ , then, as is well known,<sup>3,4</sup> the Gaussian (2) appears "reflected" in the absorption spectrum when the excited-state curve is linear, as in Fig. 2(a). In the case of a forbidden transition, the Gaussian alone does not suffice to determine the absorption curve. We must include with the probability distribution the probability that the electronic transition will occur at a given  $Q$ , i.e., we must relax the Condon approximation.<sup>3,5</sup> For transitions between two levels of the same parity, as in  $Tl^0$ , we assume that we are dealing with an odd-parity mode which can mix (say)  $s$  states into the  $p$  states. Then it is reasonable to assume that the electronic matrix element depends linearly on  $Q$ . This matrix element appears as a square in the transition probability, so we must examine the weighting function<sup>6</sup>

$$Q^2 e^{-\alpha(T)Q^2}, \quad (4)$$

which is plotted as B in Fig. 2(a). The transition probability is zero at  $Q=0$ ; the center has cubic symmetry there, so there is no transition matrix element, even though the probability distribution is at a maximum. The maxima of (4) occur at  $Q_1 = \pm 1/\alpha(T)$ , and each of them leads to absorption peaks at energies  $E_1 \pm JQ_1 - \frac{1}{2}K_0 Q_1^2 \pm \frac{1}{2}K_0 Q_1^2$ . Thus the weighted probability distribution allows us to "see" the excited-state splitting. It is also of interest to note that as  $T$  is increased, the maxima  $Q_1$  move outward, which can explain an increase in the splitting of the upper state with temperature. The total oscillator strength of this doublet also increases with  $T$  in a well-known way.<sup>7,8</sup>

<sup>4</sup> See the reviews by C. C. Klicik and J. H. Schulman, *Solid State Phys.* **5**, 97 (1957); and D. L. Dexter, *ibid.* **6**, 353 (1958).

<sup>5</sup> Considerations similar to these in the case of allowed transitions have been made by N. N. Kristoffel and G. S. Zavt, *Fiz. Tverd. Tela* **5**, 1279 (1963), [English transl.: *Soviet Phys.—Solid State* **5**, 932 (1963).]

<sup>6</sup> Equation (4) is a crude approximation in the sense that a thermal average has been taken before multiplying by  $Q^2$ . This expression is of no use, for example, in computing line shapes at  $T > 0$ , and we emphasize that its use throughout this paper is only meant to be qualitative.

<sup>7</sup> R. Kubo and Y. Toyozawa, *Progr. Theoret. Phys. (Kyoto)* **13**, 160 (1955).

<sup>8</sup> The case of NaCl:Ag has been discussed by the author: R. S. Knox, *J. Phys. Soc. Japan* **18**, Suppl. II, 268 (1963).

TABLE I. Observed and calculated splittings and total relative oscillator strengths in the  $Tl^0(^2P_{1/2} \rightarrow ^2P_{3/2})$  transitions in KCl. Numbers in parentheses are used to fit parameters and predict the 77°K number.

$T$ (°K)	Splitting (eV)			$10^4 \times$ Total oscillator strength	
	Expt. <sup>a</sup>	Theor. <sup>b</sup>	Theor. <sup>c</sup>	Expt. <sup>a</sup>	Theor. <sup>d</sup>
4	0.112	(0.112)	(0.112)	1.00	(1.00)
77	0.150	0.146	0.117	1.67	1.57
153	0.196	(0.196)	(0.196)	2.76	(2.76)

<sup>a</sup> From Delbecq, Ghosh, and Yuster, Ref. 1.

<sup>b</sup> Fitted by the "linear theory" of Sec. II.

<sup>c</sup> Fitted by the "quadratic theory" mentioned in Sec. III.

<sup>d</sup> Fitted by Eq. (6) and essentially independent of the form of excited state curves.

If we approximate the odd-parity mode involved as the odd-parity longitudinal mode of a triatomic linear molecule, with the  $Tl^0$  and two nearest neighbors participating, we may use a reduced mass  $M = [(2M_{Cl})^{-1} + M_{Tl}^{-1}]^{-1}$ . Taking a linear excited-state splitting ( $\Delta_0 = K_e = 0$ ) to fit the temperature dependence of the splitting observed in Ref. 1, we have only two unknowns, namely  $J_e$  [Eq. (1)] and  $\omega$ ; and their respective values turn out to be 0.32 eV/ $a_0$  ( $a_0 = 0.53 \times 10^{-8}$  cm) and  $1.4 \times 10^{13}$  sec<sup>-1</sup> ( $\hbar\omega/k_B = 103^\circ\text{K}$ ). These two values are obtained by fitting

$$\begin{aligned} E^+[Q_1(T)] - E-[Q_1(T)] \\ &= 2J_e Q_1(T) \\ &= 2J_e \alpha(T)^{-1} \\ &= 2J_e [(\hbar/M\omega) \coth(\hbar\omega/2k_B T)]^{1/2} \end{aligned} \quad (5)$$

at  $T=4$  and  $153^\circ\text{K}$ ; the splitting at  $77^\circ\text{K}$  is then predicted to within 1% (Table I). Similarly, using Kubo and Toyozawa's oscillator-strength expression<sup>7</sup>

$$f(T) = f_0 \coth(\hbar\omega/2k_B T), \quad (6)$$

we find that the observed values of the integrated absorption cross section may be fitted with  $\hbar\omega/k_B = 117^\circ\text{K}$ , in reasonably good agreement with that obtained from the splitting. The accuracy of the mode frequency deduced is not too high, however. A 10% error in the splittings results in a 20% error in  $\hbar\omega/k_B$ .

One is tempted to conclude that a single configuration coordinate model with linear excited-state splitting is capable of explaining the experimental data quite well. However, several qualifications must be made, as noted in the next section.

### III. DISCUSSION

The vast qualitative usefulness of single-configuration-coordinate models in interpreting absorption and luminescence phenomena has recently been taxed to its limit by accurate spectral measurements, and several authors have been forced to develop theories including two or more coordinates explicitly.<sup>9,10</sup> The single-

<sup>9</sup> Y. Toyozawa, Technical Report of the Institute of Solid State Physics, University of Tokyo, Report No. A119, 1964 (unpublished); H. Mahr, *Phys. Rev.* **132**, 1880 (1963); C. H. Henry, S. E. Schnatterly, and C. P. Slichter, *ibid.* **137**, A602 (1965); P. R. Moran, *ibid.* **137**, A1016 (1965).

<sup>10</sup> T. H. Keil, *Phys. Rev.* **140**, A601 (1965).

coordinate theory of part II of the present note stretches one's credulity in spite of its qualitative success. First, one cannot generally produce a linear splitting of a degenerate state of definite parity with a mode of arbitrary symmetry. Thus parabolic excited-state curves [Fig. 2(b)] might be somewhat more realistic but the fit to the data is worse (see Table I); and the excited-state force constant  $K_e$  must be chosen several times larger than the corresponding ground-state quantity (9 eV  $a_0^{-2}$  and 1.4 eV  $a_0^{-2}$ , respectively). This ratio would make a one-mode semiclassical theory untenable, since quantization of the excited-state vibrational wave functions would be necessary.<sup>10</sup> This objection is mitigated somewhat, though certainly not eliminated, by the observation that the frequencies we are discussing may be better regarded as effective ("reduced") frequencies, in the sense that our "coth" expressions are approximations to linear combinations of "coth" expressions for different frequencies which would appear in a many-coordinate model. We must also note that the single mode used in Sec. II as a specific example is only one of three degenerate modes, i.e., we were dealing with excitations of a three-dimensional harmonic oscillator in cubic surroundings. We may say one thing in defense of the single-coordinate linear theory, namely, that it certainly could be both reasonable and correct if the excited state were truly Stark split by the mode  $Q$ . This would be the case if, in the present example, say, the  ${}^2P_{3/2}$  term were closely degenerate with some  ${}^2S_{1/2}(\Gamma_6)$  term, which would have to enter as a charge-transfer-like state since the atom exhibits no such close state.

An alternative suggestion by Cohen<sup>2</sup> (see also Moran, Ref. 9, in a different context) alleviates the difficulties with the pure quadratic model. He attributes the splitting of the  ${}^2P_{3/2}$  state, which normally is not split in a cubic system in the crystal-field sense, to a dynamical Jahn-Teller effect, i.e., to strong interaction of the degenerate excited electronic state with a degenerate mode  $Q'$ , in particular, a mode of  $\Gamma_3(E_1)$  symmetry. (In one of the partners of this doubly degenerate mode, four neighbors move inward while two opposite neighbors move outward.) Since this is an even-parity mode, the transition would still be completely forbidden. Thus we *must* admit at least one more mode, such as our assumed odd-parity mode; and the energy of the system must be represented in a two-dimensional configuration-coordinate diagram (Fig. 3). The effect of any such Jahn-Teller splitting may be approximated in our semiclassical model by separating the two excited-state energy surfaces at the origin. Figure 2(c), which we have discussed earlier, may be interpreted in this context as a section of all these sheets in the plane  $Q'=0$ . This suggests that the observed splitting  $\Delta$  be fitted to

$$\Delta = \Delta_0 + (\hbar K_e / M\omega) \coth(\hbar\omega / 2k_B T), \quad (7)$$

where  $\omega$  is still a frequency associated with odd-parity mode. We now have three parameters to fit to the data at three points, and the results are  $\Delta_0 = 0.08$  eV,  $\hbar\omega/k_B = 80^\circ\text{K}$  ( $\omega = 1.05 \times 10^{13}$  sec<sup>-1</sup>), and  $K_e = 2$  eV/ $a_0^2$ . The

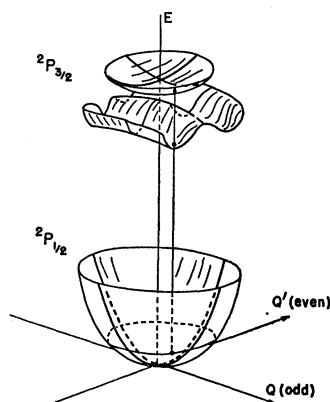


FIG. 3. A more general description of the energy of the system.  $Q'$  is a normal-mode coordinate which interacts strongly with the  ${}^2P_{3/2}$  states, possibly splitting them at  $Q'=0$  by the dynamical Jahn-Teller effect (Cohen, Ref. 2; Moran, Ref. 9).

rather low value of  $\omega$ , which places it within the acoustic band of KCl, indicates that  $Q$  must represent an in-band resonance or merely the collective effect of all the crystal odd-parity modes at the Ti<sup>0</sup> site (as was the case above). Nonetheless,  $\omega$  is of the order of magnitude of the effective breathing mode frequency<sup>4</sup> for line broadening in KCl:Ti<sup>+</sup> ( $\omega = 2\pi\nu_0 = 1.6 \times 10^{13}$  sec<sup>-1</sup>) and the effective frequency derived above from the oscillator-strength temperature dependence. Finally, we note that  $K_e$  again implies a larger excited-state curvature than that of the ground state and a quantum treatment of the excited states is in order. Indeed, there is vibrational structure in the higher energy peak of the Delbecq-Ghosh-Yuster data at 4°K, as the quantum treatment would predict.

In the system NaCl:Ag<sup>+</sup>, a similar temperature-dependent splitting is observed in the parity-forbidden 5.82 and 5.92 eV absorption lines.<sup>8</sup> The present model is certainly simpler and probably more workable than the rather elaborate one proposed in Ref. 8, which involved superposition of two different electronic transitions for the 5.82-eV line.

#### IV. CONCLUSIONS

The observed splitting of the  ${}^2P_{3/2}$  level of KCl:Ti<sup>0</sup> and its apparent temperature dependence have been explained qualitatively in the following terms. There are assumed to exist excited-state energy surfaces with some increasing energy difference as a function of a certain configuration coordinate  $Q$  (Fig. 2). The assumption that these curves represent energies of final states in electronic transitions makes the treatment "semiclassical." As the temperature increases, the most probable transitions occur at increasingly large values of  $Q$  because, in our model,  $Q$  is the amplitude of an odd-parity mode which allows the otherwise forbidden transition to occur. Although the exact form of the excited-state curves will depend on several physical circumstances (degeneracy with  $s$  configurations, dynamical Jahn-Teller effect, etc.), the splitting is predicted to occur in any event. It is pointed out that a similar effect may also have been observed in the NaCl:Ag<sup>+</sup> system.