Quantum corrections to the semiclassical temperature scale in the structured emission of tetrahedral complexes

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Tetrahedral complexes with an excited state consisting of two closely lying triplet states are considered together with the full interaction Hamiltonian, including ligand field, Jahn-Teller, pseudo-Jahn-Teller, and spin-orbit interactions. The emission band shape is numerically calculated using Monte Carlo integration. The numerical calculations are applied to the $PbWO_4$ system. Previous results using a semiclassical distribution function gave reasonable line shapes, but a mismatch with physical temperature. Using the correct quantum distribution function full correspondence with physical temperature is achieved.

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I. INTRODUCTION

In previous work¹ we performed a general theoretical analysis of tetrahedral complexes of the type $(MO_4)^{q-}$ (M = V, Cr, Mo, W, Mn; q = 1-3) in which the lowest excited state consists of two closely lying triplet levels. Such complexes have been extensively studied,^{2,3} both experimentally and theoretically. Nevertheless, renewed interest in the PbWO₄ (PWO) crystal (for a review, see Ref. 4), in particular its peculiar experimentally observed triple-peak emission spectra,⁵ necessitated a complete numerical analysis of the complex adiabatic potential energy surfaces (APES's) of tetrahedral complexes in order to better understand their optical characteristics.

The full interaction Hamiltonian includes ligand field (LF), Jahn-Teller (JT), pseudo-Jahn-Teller (PJT), and spinorbit (SO) interactions. We analyzed the resulting APES's and numerically calculated the emission spectra of the system. The calculation was performed within the semiclassical approach of Toyozawa and Inoue,⁶ using Monte Carlo numerical integration. The calculated spectra were then qualitatively compared to the experimental emission band shape of PWO. Semiquantitative agreement was obtained. Some disagreements were discussed. The main discrepancy between calculated and observed spectra was in the temperature dependence. Although spectral structure becomes less sharp with increasing temperature both theoretically and experimentally, the actual temperatures at which this occurred were too low theoretically. We pointed out¹ that the temperature that enters the calculation within the semiclassical approximation is not the physical temperature but a sort of effective temperature, which is in fact lower than the real one.

In the present paper we show that this discrepancy in the temperature dependence of the calculated spectra can be removed by a quantum approach. We calculate the emission bands using both semiclassical and quantum formulas and show the difference in their temperature dependence. The numerical calculation is again applied to PWO.

II. THEORY

According to molecular orbital calculations,^{3,7} the lowest excited state of the closed-shell ions $(MO_4)^{q^-}$ in T_d symmetry consists of the 3T_1 and 3T_2 states separated by an energy gap Δ , which is expected to be small. As discussed in Ref. 1, the total Hamiltonian of the problem that we consider is

$$H_{\rm TOT} = H_{\rm LF} + H_{\rm JT} + H_{\rm PJT} + H_{\rm SO}, \qquad (1)$$

where $H_{\rm LF}$, $H_{\rm JT}$, $H_{\rm PJT}$, $H_{\rm SO}$, are ligand field, JT interaction, PJT interaction, and SO coupling, respectively. We chose X, Y, Z, and ξ , η , ζ as the orbital basis functions for the ${}^{3}T_{1}$ and ${}^{3}T_{2}$ states, respectively, and $S_{\rm x}$, $S_{\rm y}$, $S_{\rm z}$ as the triplet spin functions. The total spin-orbital problem leads to an 18×18 Hamiltonian matrix with the basis functions

$${}^{3}T_{1}:|XS_{i}\rangle, |YS_{i}\rangle, |ZS_{i}\rangle,$$

 $T_{2}:|\xi S_{i}\rangle, |\eta S_{i}\rangle, |\zeta S_{i}\rangle, i=x,y,z.$ (2)

For details of the Hamiltonian matrix construction see Ref. 1. We retain the notation of Ref. 1: λ is the spin-orbit coupling parameter, *a*, *b*, *c* (K_{α} , K_{ϵ} , K_{τ}) are the linear JT coupling coefficients (force constants) to totally symmetric, tetragonal, and trigonal modes, b_{12} and c_{12} are the pseudo-JT coupling to tetragonal and trigonal modes, and W_0 is the vertical energy spacing between the ground and excited ${}^{3}T_{2}$ state. Within the semiclassical approach of Ref. 1 and assuming no change in the force constants (about which we comment later), the normalized line-shape function of the optical emission ${}^{3}T_{1,2} \rightarrow A_1$ may be written

$$f(E) = \left(\frac{K_{\alpha}}{2\pi k_{B}T}\right)^{1/2} \left(\frac{K_{\epsilon}}{2\pi k_{B}T}\right) \left(\frac{K_{\tau}}{2\pi k_{B}T}\right)^{3/2} \\ \times \sum_{i}^{6} \int \cdots \int dQ_{1} dQ_{2} \cdots dQ_{6} |\langle g_{j} | \mathbf{M} | e_{i} \rangle|^{2} \\ \times \exp\left(-\frac{K_{\alpha}}{2k_{B}T} (Q_{1} - Q_{1}^{0})^{2} - \frac{K_{\epsilon}}{2k_{B}T} [(Q_{2} - Q_{2}^{0})^{2} \\ + (Q_{3} - Q_{3}^{0})^{2}] - \frac{K_{\tau}}{2k_{B}T} [(Q_{4} - Q_{4}^{0})^{2} + (Q_{5} - Q_{5}^{0})^{2} \\ + (Q_{6} - Q_{6}^{0})^{2}]\right) \delta(E - X_{ij}(Q_{1}, Q_{2}, \cdots , Q_{6})), \quad (3)$$

where *E* is the photon energy, k_BT is the thermal energy, $\langle g_j | \mathbf{M} | e_i \rangle$ is the dipole matrix element between the components of the excited (e_i) and ground (g_j) electronic states, and $(Q_1^0, Q_2^0, \ldots, Q_6^0)$ are the coordinates of the minimum on the excited state APES. The transition energies X_{ij} are computed by numerically diagonalizing the Hamiltonian (1). Equation (3) is essentially a constrained (by the δ function) Boltzmann factor, and provides the probability that at a given temperature the system is found with coordinates Q_1, Q_2, \ldots .

In the present paper we introduce the quantum version of Eq. (3). First consider a simpler case. In one dimension, the Boltzmann factor for being at a point Q at temperature T, $\sqrt{K/2\pi k_B T} \exp(-KQ^2/2k_B T)$, is replaced by^{8,9}

$$\left[\frac{m\omega}{\hbar\pi}\tanh\left(\frac{\hbar\omega}{2k_BT}\right)\right]^{1/2}\exp\left[-\frac{m\omega}{\hbar}Q^2\tanh\left(\frac{\hbar\omega}{2k_BT}\right)\right].$$

Similarly, the quantum emission band-shape function, Eq. (3), becomes

$$f(E) = \left[\frac{m_{\alpha}\omega_{\alpha}}{\hbar\pi} \tanh\left(\frac{\hbar\omega_{\alpha}}{2k_{B}T}\right)\right]^{1/2} \left[\frac{m_{\epsilon}\omega_{\epsilon}}{\hbar\pi} \tanh\left(\frac{\hbar\omega_{\epsilon}}{2k_{B}T}\right)\right]$$

$$\times \left[\frac{m_{\tau}\omega_{\tau}}{\hbar\pi} \tanh\left(\frac{\hbar\omega_{\tau}}{2k_{B}T}\right)\right]^{3/2} \sum_{i}^{6} \int \cdots \int dQ_{1}dQ_{2}$$

$$\cdots dQ_{6} |\langle g_{j}|\mathbf{M}|e_{i}\rangle|^{2} \exp\left[-\frac{m_{\alpha}\omega_{\alpha}}{\hbar} \tanh\left(\frac{\hbar\omega_{\alpha}}{2k_{B}T}\right)\right]$$

$$\times (Q_{1} - Q_{1}^{0})^{2} - \frac{m_{\epsilon}\omega_{\epsilon}}{\hbar} \tanh\left(\frac{\hbar\omega_{\epsilon}}{2k_{B}T}\right) \{(Q_{2} - Q_{2}^{0})^{2}$$

$$+ (Q_{3} - Q_{3}^{0})^{2}\} - \frac{m_{\tau}\omega_{\tau}}{\hbar} \tanh\left(\frac{\hbar\omega_{\tau}}{2k_{B}T}\right) \{(Q_{4} - Q_{4}^{0})^{2}$$

$$+ (Q_{5} - Q_{5}^{0})^{2} + (Q_{6} - Q_{6}^{0})^{2}\}\right]$$

$$\times \delta(E - X_{ij}(Q_{1}, Q_{2}, \cdots Q_{6})), \qquad (4)$$

where m_i , ω_i $(i = \alpha, \epsilon, \tau)$ are the effective masses and frequencies of the associated vibrational modes. Note that for high temperature Eq. (4) goes over to Eq. (3), bearing in mind the relation



FIG. 1. Cross section along the Q_4 axis ($Q_4 = Q_5 = Q_6$; $Q_2 = Q_3 = 0$) of all APES's on the 3T_1 and 3T_2 level showing the trigonal minima. Parameters used in the calculation are: $\Delta = 0$, $\lambda = 0.07$ eV, b = 0, c = 1.2 eV/Å, $b_{12} = 0.1$, $c_{12} = 0.15$, $K_{\epsilon} = 2.2$ eV/Å², $K_{\tau} = 2.2$ eV/Å².

$$K_i = m_i \omega_i^2 \,. \tag{5}$$

III. RESULTS AND DISCUSSION

The numerical calculation was performed as in Ref. 1 Because comparison to PbWO₄ was desired, we considered the case where trigonal JT minima in the lowest excited state of PWO split into three APES's, which occurs for $\Delta \approx 0$. For the desired intensity relations among the components contributing to the emission band we assume the JT interaction to be greater than the PJT interaction (discussed in detail in Ref. 1). The APES's corresponding to that situation are shown in Fig. 1. The parameters of the WO₄ complex needed for the emission band calculation were determined as follows. For the trigonal mode frequency we used the experimental value corresponding to trigonal vibrations in the ground state;¹⁰ the elastic constants were calculated using the UBFF (Urey-Bradley force field) approximation,¹⁰ not allowing mixing between "pure" stretching and "pure" bending modes.¹¹ The effective mass of the corresponding mode was calculated from Eq. (5).

For simplicity, as in Ref. 1, we started our calculations without the electron-nuclei coupling to the totally symmetric vibrational mode α , i.e., we did not include the coordinate Q_1 . In Fig. 2 is a comparison of the temperature evolution of the emission band calculated semiclassically [Eq. (3)] and quantum mechanically [Eq. (4)]. It is evident that semiclassically the spectral structure is more sensitive to changes of temperature, and its features tend to be washed out at relatively low temperatures. Quantum mechanically, there is pronounced structure up to much higher temperatures.

In Ref. 1 we demonstrated that the total width of the spectrum and its smoothing are also affected by the following three factors: the totally symmetric coordinate Q_1 , the spatial separation of the ground- and excited-state minima in Q_i space, and the higher elastic constant of the ground state



FIG. 2. Normalized emission spectra for the $({}^{3}T_{1}, {}^{3}T_{2}) \rightarrow A_{1}$ transition. Parameters used in the calculation are: $\Delta = 0$, $\lambda = 0.07$ eV, b = 0, c = 1.2 eV/Å, $b_{12} = 0.1 \text{ eV/Å}$, $c_{12} = 0.15 \text{ eV/Å}$, $K_{\epsilon} = 2.2 \text{ eV/Å}^{2}$, $K_{\tau} = 2.2 \text{ eV/Å}^{2}$, $\hbar \omega_{\epsilon} = 0.04 \text{ eV}$; $\hbar \omega_{\tau} = 0.04 \text{ eV}$; $W_{0} = 3.8 \text{ eV}$ (Ref. 12); (a) semiclassical calculation: solid line T = 4 K, dotted line T = 70 K, dashed line T = 90 K, long-dashed line T = 150 K. (b) Quantum-mechanical calculation: solid line T = 300 K, dotted line T = 150 K, dashed T = 200 K, long-dashed line T = 300 K. Spectra for different temperatures are vertically shifted for better visualization.

with respect to the excited state. Figure 3 displays the temperature evolution of the emission spectra using the semiclassical and the quantum-mechanical formula with these additional considerations. Recalling Fig. 2 of Ref. 1 we note that the quantum approach [Fig. 3(b)] considerably improves agreement with experiment, including our ability to use true temperature in our calculations.

As stated above, we calculated emission spectra using the frequencies and force constants of the undistorted configuration. It is known that in the distorted relaxed excited state those quantities change (see, e.g., Refs. 13 and 14). In fact, our calculational method provides us with the new force constants,¹⁵ which we find to be in general agreement with previous results.¹⁴ Our calculation also shows the distorted force constants to be well separated from zero (which is certainly not always the case, cf. Refs. 16 and 17), indicating that this is not a regime where tunneling is important. However, we did not feel that additional precision in this part of the calculation would enhance our results.¹⁸ Our principle achievement is the explanation of the PWO triple peak structure using JT, PJT, and SO interactions. We emphasize that



FIG. 3. Normalized emission spectra for the $({}^{3}T_{1}, {}^{3}T_{2}) \rightarrow A_{1}$ transition. The calculation is performed by taking into account the spatial separation of the ground state from the excited state (K_{g} stands for the elastic constant of the ground state) and the totally symmetric coordinate Q_{1} . Parameters used in the calculation are: $\Delta = 0$, $\lambda = 0.07$ eV, a = 0.7 eV/Å, b = 0, c = 1.2 eV/Å, $b_{12} = 0.1$ eV/Å, $c_{12} = 0.15$ eV/Å, $K_{\alpha} = 2.2$ eV/Å², $K_{\epsilon} = 2.2$ eV/Å², $K_{\tau} = 2.2$ eV/Å², $K_{g} = 2.5$ eV/Å²; $\hbar \omega_{\alpha} = 0.04$ eV, $\hbar \omega_{\epsilon} = 0.04$ eV, $\hbar \omega_{\tau} = 0.04$ eV, $W_{0} = 4.5$ eV (Ref. 12); (a) semiclassical calculation: solid line T = 4 K, dotted line T = 10 K, dashed line T = 15 K, long-dashed line T = 100 K; (b) quantum-mechanical calculation: solid line T = 300 K. Spectra for different temperatures are vertically shifted for better visualization.

our explanation is offered at the qualitative level; we do not claim detailed matching of the data. In fact we ourselves would be skeptical of small improvements obtained through better force constants or frequencies, especially in view of the latitude (albeit small) in the choice of parameters of the Hamiltonian.

IV. CONCLUSION

In this paper we solved the main problem found in our previous work where although the qualitative progression of structural features was well fit with increasing temperature, the actual temperature values at which the changes occurred did not match experiment. We have here shown that the semiclassical formula is responsible for this discrepancy, and using the appropriate quantum-mechanical formula we obtain realistic results corresponding to observation. It is interesting that the quantum formula must be used even at one might have considered to be relatively high temperatures. This sensitivity arises from the argument of the hyperbolic tangent, $\hbar \omega/2k_BT$, in the quantum formula, Eq. (4). The conclusion one should draw from this is that even at room

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temperature ($2k_BT \sim 52 \text{ meV}$) one may still need a quantum treatment, depending on the modes of the substance.

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eigenvalues of H. Let E(Q) be the nth eigenvalue of H as a function of the six-component Q. Extrema are characterized by $\partial E/\partial Q_i = 0$, $j = 1, \dots, 6$. The usual method seeks a solution to f(x)=0 by iterating $x_{n+1}=x_n-f(x_n)/f'(x_n)$, with $x \in \mathbf{R}$. It is easy to generalize this to N dimensions as $x_{n+1} = x_n$ $-M(x_n)^{-1}f(x_n)$, where $x, f \in \mathbf{R}^N$ and $M_{ii} \equiv \partial f_i / \partial x_i$. Noting that in our case f_i is $\partial E/\partial Q_i$, the matrix M is just the Hessian. Its eigenvalues provide the new force constants. The calculation is made simpler and more reliable using the easily verified fact that $\partial E/\partial Q_i = \langle n | \partial H/\partial Q_i | n \rangle$ (i.e., derivatives of the eigenfunction drop out). Partial derivatives of H are analytically calculated and, using the numerical eigenvectors, good values for the partials of E are obtained. From these M can be calculated using differences of $\partial E/\partial Q_i$ at nearby values of Q. Thus our method for locating minima in E (for which we used the eigenvalues of M to be sure we had a minimum) already provides distorted state force constants. Finally, by examining the eigenvectors of M it is possible to associate force constants with states of particular symmetry, such as trigonal.

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