Lifetimes of Triplet States of Ti$^+$-Like Ions in O_h Symmetry—Hyperfine Effect

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The hyperfine interaction is shown to be at the origin of the finite lifetime measured for the metastable level $A_{1u}(^3T_{1u})$ of Tl$^+$-like ions in alkali halides.

It is well known that the A and B absorption bands of Tl$^+$-like ions (electronic configuration ns^2) in alkali halides are due to transitions from the ground state $^1A_{1g}$ to triplet states $^3T_{1u}$ of the excited configuration ns,np.[1] More precisely, the transitions are, for the A band, $^1A_{1g}\rightarrow T_{1u}$ (or $J=1$ states of $^3T_{1u}$) which is made allowed by spin-orbit coupling between $J=1$ states and singlet states $^1T_{1u}$, and for the B band, $^1A_{1g}\rightarrow E_u+T_{2u}$ (or $J=2$ states of $^3T_{1u}$) which is allowed by electron-lattice coupling between $J=1$ and $J=2$ states.[2] The transition into the state A_{1u} (or $J=0$ state of $^3T_{1u}$) has not been observed in absorption. This state A_{1u} plays a key role as a trap just below the emitting level T_{1u} in the dynamics of the emissions A_T and A_X (which are the reverse of the A absorption process[3]). Interestingly enough, its radiative lifetime has been measured for a number of systems. Three types of mechanisms have been proposed to explain the finite oscillator strength of the transition $A_{1u}\rightarrow {}^1A_{1g}$: (i) electron-lattice coupling mixes A_{1u} state to T_{1u} states[4] or to E_u+T_{2u} states[2]; or (ii) hyperfine interaction[5] or (iii) static perturbation[4] (strain field associated with a defect) mixes A_{1u} and T_{1u} states. Mixing of A_{1u} and T_{1u} states by orbit-lattice coupling and static perturbation involves off-diagonal matrix elements of orbital operators which could be severely reduced by the Ham effect.[6] So these mixing mechanisms can be efficient only when the spin-orbit coupling is much larger than the Jahn-Teller coupling, which is the case for the heavy ions Tl$^+$, Pb^{2+}, Bi^{3+}. On the other hand, the hyperfine interaction which couples directly the spin states (and not the orbital states) can be effective for both the heavy and light ions (Ga$^+$, In$^+$,...).

The effect of the hyperfine interaction was discussed by Fontana *et al.*[5] These authors used parameters deduced from *absorption* data to calculate the mixing of A_{1u} and T_{1u} states. As they themselves noted, the good agreement they found between the calculated and measured lifetimes in KI:Tl$^+$ "is to be taken with a grain of salt," and therefore the actual role of the hyperfine interaction on the lifetime of the A_{1u} state is still to be demonstrated. In this paper we shall examine the effect of the hyperfine interaction in light of recent progress on the knowledge of the *relaxed* excited states $^3T_{1u}$.[3,7-9] The mixing of A_{1u} and T_{1u} states will be considered in the two extreme cases of the Jahn-Teller coupling larger or smaller than the spin-orbit coupling, which apply to the light (Ga$^+$, In$^+$) and heavy (Tl$^+$) ions, respectively. Using published data on the hyperfine interaction and the temperature dependence of the lifetimes of the A_T and A_X emissions, one can deduce values of parameters entering the model. It will be shown that the present calculations can account for the observed lifetime of the A_{1u} state and also describe very well its variation under an applied magnetic field.[10]

First, let us consider the case in which the Jahn-Teller coupling to the E_g modes of vibration is much larger than the spin-orbit coupling (a similar calculation could be made for a predominant coupling to the T_{2g} modes). Each of the three tetragonal Jahn-Teller distortions is associated with a given orbital state X, Y, or Z and a triplet spin state x, y, and z of the $^3T_{1u}$ level. As a result of spin-spin interaction and the second-order effect of spin-orbit coupling,[6,11] the spin degeneracy is partially lifted leaving a singlet Xx at an energy D below a doublet (Xy, Xz) and similarly for the other orbital states. The linear combinations $Xx+Yy+Zz$ and $2Xx-Yy-Zz$ transform like the A_{1u} and E_u representations of the O_h group, respectively. Since the electric or magnetic dipole transitions from the A_{1u} or E_u states to the ground state $^1A_{1g}$ are forbidden, singlet states Xx, Yy, and Zz are expected to be very long lived. On the other hand, the linear combinations $Yz-Zy$, $Zx-Xz$, and $Xy-Yx$ transform like the X, Y, and Z components of the T_{1u} representation. They are mixed to singlet states $^1T_{1u}$ by the spin-orbit coupling so that radiative transitions from doublet states (Xy, Xz),... are then allowed with well-defined selection rules.[11,12] Ga and In nuclei have nonzero nuclear spins I and in the presence of a magnetic field H the spin Hamiltonian for the Jahn-Teller well X can be written as[8]

$$\mathcal{H}_x = DS_x^2 + \mathcal{H}_1, \tag{1}$$

$$\mathcal{H}_1 = \vec{I}\cdot\overleftrightarrow{A}\cdot\vec{S} + \mu_B(g_s\vec{S}+g_L\vec{L})\cdot\vec{H} + g_n\mu_N\vec{I}\cdot\vec{H}, \tag{2}$$

where $D S_x^2$ describes the fine structure in tetragonal symmetry and the three terms of $\mathcal{H}_1$ represent the hyperfine interaction in the $S=1$ state, the spin and orbital Zeeman interactions, and the nuclear Zeeman interaction, respectively. $g_s \simeq 2$ and g_L are the free spin and orbital g factors. If we assume $D \gg \mathcal{H}_1$, the use of the perturbation theory is valid, and the singlet Xx is at an energy D below the doublet (Xy, Xz). In first order of perturbation, the Xx state contains a small admixture [of order of $(A+\mu_B H)/D$] of Xy and Xz states. The lifetime of each hyperfine level can be obtained by straightforward calculations. If the populations of the $2I+1$ hyperfine levels associated with the Xx state are *equal*, then the average lifetime τ_M of this metastable state will be given by

$$1/\tau_M = (U+VH^2)/\tau_R, \tag{3}$$

$$U = \tfrac{2}{3}I(I+1)(A_\perp/D)^2, \quad V = (g_s\,\mu_B/D)^2(\beta^2+\gamma^2), \tag{4}$$

where τ_R is the radiative lifetime of the doublet (Xy, Xz), $A_\perp = A_{yy} = A_{zz}$, and α, β, and γ are the direction cosines of H in the coordinate axes OX, OY, and OZ. Equation (3) does not contain the cross term $A_\perp H$; this results from the assumption of equal populations among the hyperfine levels.

The same type of calculations can be done when the Jahn-Teller energy is smaller than the spin-orbit coupling. Now the metastable singlet A_{1u} $(J=0)$ lies below the radiative triplet T_{1u} $(J=1)$. If we call D their energy separation and assume again that the populations of the hyperfine levels associated with the singlet A_{1u} are equal, it can be shown that τ_M is given (for $H=0$) by

$$\frac{1}{\tau_M} = \tfrac{2}{3}I(I+1)\left(\frac{A_\perp}{D}\right)^2 f_{JT}^2\,\frac{1}{\tau_R}, \tag{5}$$

where f_{JT} is the overlap integral of the vibrational wave functions associated with A_{1u} and T_{1u} states. A more precise expression would be obtained by taking into account the mixing of the A_{1u} state with all the vibronic states associated with the T_{1u} level. Then f_{JT}^2 would be the sum of the squares of all the overlap integrals, and D would be replaced by an effective $D_{\text{eff}} > D$.

To check the calculations we need values of the parameters τ_R, D, and $A_\perp$. It will be shown below that τ_R and D can be deduced from the analysis of the temperature dependence of the lifetimes of the A_T or A_X emissions, and $A_\perp$ from EPR in the ground state $S=\frac{1}{2}$ of Tl^{2+}-like ions.

Analysis of the temperature dependence of the decay of a three-level system has been made by various authors.[4,13-15] Following the notations of Dang *et al.*[15] we consider a metastable level 1 at an energy D below a radiative level 2 and assume nonradiative transitions taking place between these levels with a downward rate k_{21} and an upward rate k_{12}. The degeneracy ratio of levels 2 and 1 is called g (= 2 in our case). We assume that the decay to the ground state is purely radiative for both levels 1 and 2 with time constants τ_M and τ_R, respectively. The decay of the emission after a pulsed excitation exhibits fast and slow components with time constants τ_f and τ_s. At very low temperatures, $kT \ll D$, it can easily be seen that $\tau_s = \tau_M$ and $1/\tau_R + k_{21}^0$, k_{21}^0 being the zero-temperature limit of k_{21}. At higher temperatures, $1/\tau_s$ follows an Arrhenius law as $1/\tau_s = [gk_{21}^0/(\tau_R k_{21}^0+1)]\exp(-D/kT)$; and for $kT \gg D$, $\tau_s = [(1+g)/g]\tau_R$ if $\tau_R \ll \tau_M$. Analyzing the data of various authors[3,8,14-16] we deduce values of τ_M, τ_R, and D for KBr:Ga^+ (A_T), KI:In^+ (A_T), and KI:Tl^+ (A_X) (see Table I).

The hyperfine interaction in the relaxed excited states ${}^3T_{1u}$ has been measured only for Ga^+ in alkali halides.[9] It is found to be nearly isotropic $(A_\parallel \simeq A_\perp)$ indicating that the main contribution to the hyperfine interaction comes from the 4s electron. For triplet states ${}^3T_{1u}$ in KCl:Ga^+, the average value $A = (A_\parallel + 2A_\perp)/3 = 0.14\ \text{cm}^{-1}$ is very close to half the value $a_{4s} = 0.29\ \text{cm}^{-1}$ determined by Baranov and Khramtsov[17] for the ground state $S=\frac{1}{2}$ in KCl:Ga^{2+} (the ratio would be exactly $\frac{1}{2}$ if the spin densities at the nucleus were the same for the 4s wave functions of Ga^+ and Ga^{2+} ions). Then it is reasonable to assume that the hyperfine tensor $\overleftrightarrow{A}$ of a (ns, np) ion is isotropic in the ${}^3T_{1u}$ states and is related to the hyperfine constant a_{ns} of the doubly ionized ion (ns) in the ground state $S=\frac{1}{2}$ by $A_\parallel = A_\perp = A = a_{ns}/2$. Table II shows values of a_{ns} determined by EPR for In^{2+} and Tl^{2+} in various host lattices, but not in KI. However, an obvious trend can be observed in the reduction of a_{ns} as the bonding within the host lattice becomes more covalent, indicating that the hyper-

TABLE I. Data on τ_R, τ_M, and D. Comparison between experiments and calculations is shown in the fourth column.

	τ_R (s)	τ_M (s)	D (cm^{-1})	$f_{\mathrm{JT}}^{-2}\tau_R/\tau_M$ Measured	Calculated	Ref.
KBr:Ga$^+$ (A_T)	8.4×10^{-6}	$>2\times10^{-4}$	3.1	$<4\times10^{-2}$	5×10^{-3}	8,15
KI:In$^+$ (A_T)	5×10^{-7}	4×10^{-4}	17.5	1.2×10^{-3}	1.7×10^{-3}	3,14
KI:Tl$^+$ (A_X)	3×10^{-8}	3×10^{-3}	240	10^{-5}	1.7×10^{-5}	16

fine coupling in KI would be close to that in KBr and ZnS. Values of A in KI:In$^+$ and KI:Tl$^+$ estimated in this way are given in the fourth column of Table II.

With values of D and A collected in Tables I and II, the ratios τ_R/τ_M are calculated using Eqs. (3) and (4) for KBr:Ga$^+$ and KI:In$^+$, and Eqs. (3) and (5) for KI:Tl$^+$. The results are shown in the fourth column of Table I and can be compared to the measured values. Given the uncertainties in the experimental values of τ_R and in the estimate of A, the agreement is quite good, especially in the case of KI:In$^+$ for which all the parameters of the model are known. For KBr:Ga$^+$ only a lower bound of τ_M is known experimentally which does not allow a precise comparison, but the upper bound observed for τ_R/τ_M is effectively larger than the calculated value. For KI:Tl$^+$ the value of the overlap integral f_{JT} is not known but is expected to be close to 1 ($f_{\mathrm{JT}} \lesssim 1$) since minima on the adiabatic potential energy surfaces associated with A_{1u} and T_{1u} states are obtained for approximately the same values of the configuration coordinates.[7] In this case our result shows that the radiative lifetime of the A_{1u} level in KI:Tl$^+$ can also be explained by the hyperfine interaction mechanism.

Magnetic field effects on the decay time of the A_T emission in KI:In$^+$ offer a further check of the calculations. Fukuda and Yuster[10] measured the variations of the time constant τ_s under an applied magnetic field $\vec{H} \parallel [111]$ at $T = 3.8$ K. They tentatively fitted the data by a law $1/\tau_s = (a + bH)^2/\tau_R$, obtaining rather poor results at low magnetic field. By plotting $1/\tau_s$ vs H^2 we find that their data are perfectly aligned on a straight line for all values of H. This shows that our Eq. (3) is valid and that the populations of the hyperfine levels associated with the metastable state can be considered as equal at $T = 3.8$ K and for $H \lesssim 50$ kG. Furthermore, taking $\beta^2 = \gamma^2 = \frac{1}{3}$, analysis of these data with Eqs. (3) and (4) yields $\tau_R = 8.5\times10^{-7}$ s and $A = 0.21$ cm^{-1} which are in fair agreement with $\tau_R = 5\times10^{-7}$ s (determined by Klick and Drickamer[14]) and $A = 0.16$ cm^{-1} (estimated from EPR results of Raüber and Schneider[18]).

In conclusion, the hyperfine interaction has been shown here as the main mechanism for the radiative decay of the metastable state A_{1u} of

TABLE II. Hyperfine interaction constants a_{ns} of isotopes ^{69}Ga, ^{115}In, and ^{205}Tl in the ground state $S = \frac{1}{2}$. A is the estimated value in the excited state $^3T_{1u}$ (see text).

	Configuration	I	a_{ns} (cm^{-1})	A (cm^{-1}) (estimated)	Ref.
KBr:Ga$^+$	$4s, 4p$	3/2		0.14[a]	8
Free ion In^{2+}	$5s$	9/2	0.73		
ZnS:In^{2+}			0.32		18
KI:In$^+$	$5s, 5p$			0.16	
Free ion Tl^{2+}	$6s$	1/2	5.87		19
KCl:Tl^{2+}			3.52		20
KBr:Tl^{2+}			3.05		21
ZnS:Tl^{2+}			2.4		19
KI:Tl$^+$	$6s, 6p$			1.4	

[a] Directly measured by EPR in the excited state $^3T_{1u}$.

Tl$^+$-like phosphors. It is striking that this mechanism applies for two opposite physical situations, Jahn-Teller coupling larger or smaller than spin-orbit coupling. The importance of the hyperfine interaction in the dynamics of the emission has also been illustrated by recent studies of the polarization of the emission under polarized excitation light.[12] The knowledge of the hyperfine interaction and of the Jahn-Teller coupling in the excited states ${}^3T_{1u}$ is now good enough to devise a scheme for nuclear orientation by optical pumping as was done years ago for mercury vapor.[22]

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KH_2PO_4 in a Field: A Transition without Critical Microscopic Fluctuations

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Light scattering on potassium dihydrogen phosphate demonstrates that the ordering electric field reduces the isothermal microscopic response. At the continuous transition occurring at the critical field no microscopic critical fluctuation exists (no diverging correlation range) and only macroscopic thermodynamic quantities can diverge classically. This general effect for symmetry-nonbreaking elastic transitions is caused in potassium dihydrogen phosphate by higher than bilinear strain-polarization couplings in the free energy.

Potassium dihydrogen phosphate (KDP) (KH_2PO_4) experiences a slightly discontinuous paraelectric (PE) to ferroelectric (FE) transition at $T_{tr} \simeq 122$ K.[1] The ferroelectric mode softens towards the extrapolated clamped Curie temperature T_C. The noncentrosymmetric PE phase (point group $\bar{4}2m$) has a nonzero h_{63} piezoelectric constant which couples the polarization $P_3 \equiv P$ to the e_6 shear strain. This produces a soft elastic branch with stability limit at the extrapolated free Curie