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TWO-PHOTON EXCITATION SPECTRA OF Cr^{3+}:K_2NaScF_6

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Two-photon excitation (TPE) spectra of Cr^{3+}:K_2NaScF_6 exhibit unexpected features including a forbidden transition, extended progressions, a split zero-phonon line and anomalous polarization anisotropy. These features are explained by departures from standard approximations.

Keywords: Two-photon excitation; Transition-metal complex; Chromium

1. INTRODUCTION

Two-photon excitation (TPE) spectra of $Cr^{3+}:K_2NaScF_6$, excited by a Raman-shifted, Nd:YAG-pumped tunable dye laser, were recorded as functions of transition energy and polarization. Within the closure [1], Born–Oppenheimer, harmonic and crude-adiabatic approximation, the expected transition probability is given by

$$W_{a\to b} = [F(I,\omega)/\Delta^2] \times |\langle b|(\hat{\eta}\cdot\mathbf{P})^2|a\rangle|^2 G(\Omega), \tag{1a}$$

$$F(I,\omega) = \left(\frac{n^2+2}{3n^3}\right)\left(\frac{2\pi e^4 I^2}{\varepsilon_0^2 c^2 m^4 \hbar^4 \omega^4}\right), \tag{1b}$$

$$G(\Omega) = \mathrm{Av}_{\{\alpha_k\}} \sum_{\{\beta_k\}} \prod_k |\langle \chi_{b\beta_k}|\chi_{a\alpha_k}\rangle|^2 \delta\left[\sum_k(\beta_k-\alpha_k)\omega_k - \Omega\right], \tag{1c}$$

$$\Omega = 2\omega - \Omega_0. \tag{1d}$$

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The $^4A_2 \rightarrow {}^4T_2$ transition is forbidden, and the $^4A_2 \rightarrow {}^4T_{1a}$ transition is allowed with predicted polarization anisotropy in cubic symmetry [2]

$$I \propto I_0^2 \sin^2(2\phi), \mathbf{k} \parallel \langle 001 \rangle. \tag{2}$$

However, the recorded TPE spectra exhibit several unexpected features. A weak TPE spectrum of the symmetry-forbidden $^4A_2 \rightarrow {}^4T_2$ transition is observed without a zero-phonon line. The symmetry-allowed TPE spectrum of the $^4A_2 \rightarrow {}^4T_{1a}$ transition has anomalously extended vibrational progressions [3] and a weak, split zero-phonon line with anomalous polarization anisotropy. These observations are explained in terms of theoretical models involving departures from the stated approximations.

2. PHONON-ASSISTED TRANSITIONS

The appearance of a weak TPE spectrum of the symmetry-forbidden $^4A_2 \rightarrow {}^4T_2$ transition can be explained as a manifestation of phonon assistance [4], corresponding to relaxation of the crude adiabatic approximation,

$$\psi_{nv}(\mathbf{r}, \mathbf{Q}) = \phi_n(\mathbf{r}, \mathbf{Q}) \prod_k \chi_{nv_k}(Q_k), \tag{3a}$$

$$\phi_n(\mathbf{r}, \mathbf{Q}) \cong \phi_n(\mathbf{r}, \mathbf{0}) + \sum_k Q_k \sum_{l \neq n} \frac{\phi_l(r, 0) \langle l | V_k | n \rangle}{\hbar(\omega_l - \omega_n)}. \tag{3b}$$

The resulting transition probability for coupling to a single mode has the form

$$\begin{aligned} W_{a \rightarrow b} &\propto \sum_{\beta=0}^{\infty} |\langle \chi_{b\beta} | Q | \chi_{a0} \rangle|^2 \, \delta(\beta\omega_0 - \Omega) \\ &= \left(\frac{\hbar}{2\omega_0}\right) \exp(-S) \sum_{\beta=0}^{\infty} (\beta - S)^2 (S^{\beta-1}/\beta!) \delta(\beta\omega_0 - \Omega), \end{aligned} \tag{4}$$

which differs from that for an allowed transition,

$$G(\Omega) = \exp(-S) \sum_{\beta=0}^{\infty} (S^\beta/\beta!) \delta(\beta\omega_0 - \Omega). \tag{5}$$

The enabling mode must be asymmetric to ensure that the symmetry of the intermediate state in Eq. (3b) differs from that of both initial and final states. In the present case, the enabling mode appears to be an e_g mode. The zero-phonon line must vanish when both e_g coordinates are considered, since the lowest vibronic states of a Jahn-Teller system share the symmetry of the degenerate electronic states from which they are derived [5].

3. ANOMALOUSLY EXTENDED PROGRESSIONS

Vibrational progressions observed in the symmetry-allowed $^4A_2 \rightarrow {}^4T_{1a}$ TPE spectrum, corresponding to phonon frequencies of $106\,\text{cm}^{-1}$ and $310\,\text{cm}^{-1}$, are remarkable not only for their persistence but also for their resolution. As many as thirty-five phonon replicas can be distinguished in the former progression. These extended progressions are explained by electron-lattice coupling in intermediate states, obscured by the closure approximation. When this approximation is relaxed, the transition probability is modified by an additional term

$$\Delta W_{a\rightarrow b} = \left[\frac{F(I,\omega)}{\Delta^2}\right] \times \left(\frac{\omega_q}{\Delta}\right)^2 |\langle b|\hat{\eta}\cdot\mathbf{P}|c\rangle\langle c|\hat{\eta}\cdot\mathbf{P}|a\rangle|^2$$
$$\times \prod_{k\neq q} |\langle \chi_{b0_k}|\chi_{c0_k}\rangle\langle\chi_{c0_k}|\chi_{a0_k}\rangle|^2$$
$$\times \sum_{\beta=0}^{\infty} \exp(-S)\left(\frac{\gamma^2 S^\gamma}{\gamma!}\right)\delta(\beta\omega_q - \Omega), \tag{6a}$$

$$\gamma = S + \beta - 2\sqrt{S\left(\beta - \frac{1}{2}\right)}, \tag{6b}$$

where we have considered a single intermediate state c, coupled to a single mode q. Equation (6b) is an approximation based on the maximum overlap of vibrational wave functions in intermediate and final states, corresponding to coincidence of their classical turning points. The progression of Eq. (6a) is compared with that of Eq. (5) in Figure 1. The required intermediate state is a diffuse $^4T_{2u}$ state, derived from the ground $^4A_{2g}$ state by a $3d \rightarrow 4p$ substitution, coupled to zone-center t_{2g} lattice modes.

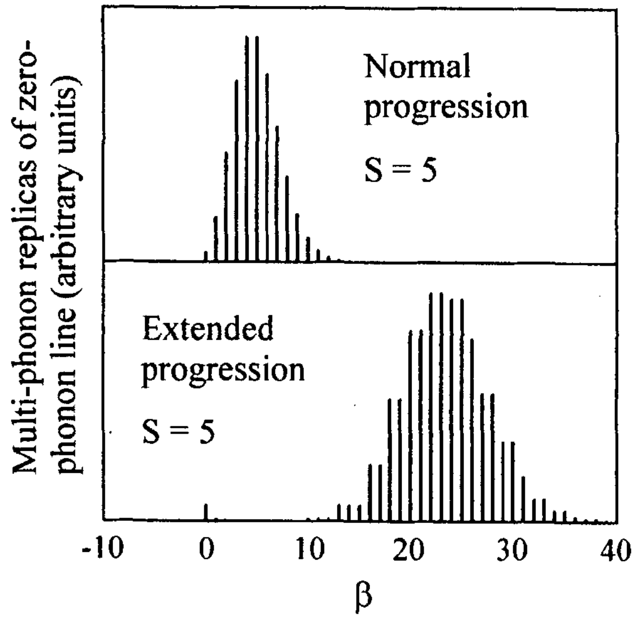

FIGURE 1 Normal and extended progressions from Eqs. (5) and (6), respectively.

4. ANOMALOUS POLARIZATION ANISOTROPY

The split zero-phonon line of the $^4A_2 \to {}^4T_{1a}$ TPE spectrum is attributed to a low temperature phase transition of Cr^{3+}: K_2NaScF_6 involving librational instability [6–8]. Counter-rotating displacements of adjoining octahedra explain anomalous polarization anisotropy as well. Averaged over domain orientations, the predicted polarization anisotropy for light propagating along $\langle 100 \rangle$ is given by

$$I(\phi) \propto I_0^2\{4\ \sin^2(2\phi) + \sin^2[2(\phi - \phi_0)] + \sin^2[2(\phi + \phi_0)]\}, \qquad (7a)$$

with intensity ratio

$$R(\phi_0) \equiv \frac{I_{\max}}{I_{\min}} = \frac{2 + \cos^2(2\phi_0)}{\sin^2(2\phi_0)}. \qquad (7b)$$

The value of this ratio for the predicted rotation [6] is $R(19.8^\circ) = 6.38$, in rough agreement with that observed for the broad band, $R(16.6^\circ) = 9.0$. A much smaller value is observed for the zero-phonon line, $R(35.6^\circ) = 2.35$. The rotation angle is increased to accommodate bond stretching in the $^4T_{1a}$

TABLE I Optimized parameters for Figure 2

Mode	*ω (cm⁻¹)*	*S*	*σ (cm⁻¹)*
e_g	449*	1.3	120
a_{1g}	542*	1.3	120

*From low-temperature emission spectra.

excited state; it is manifest as coupling to a soft t_{1g} mode, which accounts for the weakness of the zero-phonon line.

5. SIMULATED LINE SHAPES

Line shapes were simulated for both transitions by replacing the δ-functions in Eqs. (4) and (5) by normalized gaussian functions,

$$\delta(\beta\omega_0 - \Omega) \rightarrow \frac{\exp[-(\Omega - \beta\omega_0)^2/2\beta\sigma^2]}{\sigma\sqrt{2\beta\pi}}. \tag{8}$$

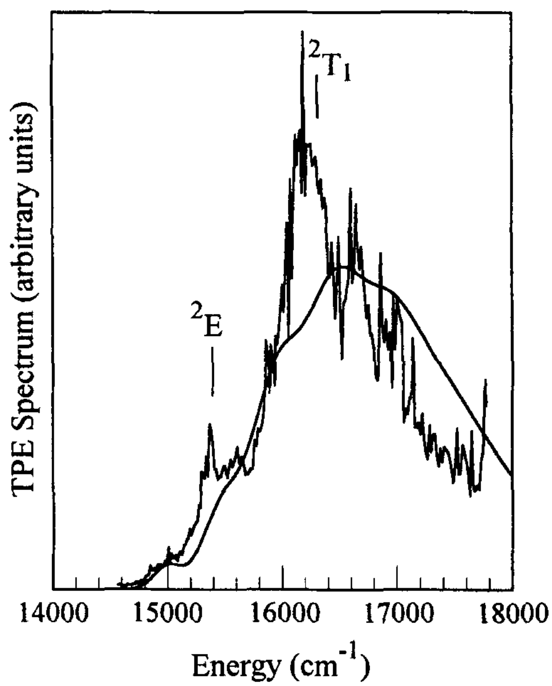

FIGURE 2 Comparison of simulated phonon-assisted line-shape function with $^4A_2 \rightarrow {}^4T_2$ TPE spectrum multiplied by ω^4. Positions of doublet-state antiresonances are also indicated.

A simulation based on parameter values listed in Table I, with the zero-phonon line suppressed, is compared with the recorded $^4A_2 \rightarrow {}^4T_2$ TPE spectrum in Figure 2.

Acknowledgment

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References

[1] Axe, J. D. Jr., (1962) *Phys. Rev.* **136**, A42.
[2] Bader, T. R. and Gold, A. (1968) *Phys. Rev.* **171**, 997.
[3] Chien, R. L., Berg, J. M., McClure, D. S., Rabinowitz, P. and Perry, B.N. (1986) *J. Chem. Phys.* **84**, 4168.
[4] Honig, B. Jortner, J. and Szöke, A. (1967) *J. Chem. Phys.* **46**, 2714.
[5] Ham, F. S. (1965) *Phys. Rev.* **138**, A1727.
[6] Sliwczuk, U. Rinzler, A. G., Kappers, L. A. and Bartram, R. H. (1991) *J. Phys. Chem. Solids* **52**, 363.
[7] Sinkovits, R. S. and Bartram, R. H. (1991) *J. Phys. Chem. Solids* **52**, 1137.
[8] Dolan, J. F., Rinzler, A. G., Kappers, L. A. and Bartram, R. H. (1992) *J. Phys. Chem. Solids* **53**, 905.