

Electronic and Molecular Structure of Transition Metal Complexes

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Abstract: The work of the group is centred on the interplay between the electronic and molecular structure of transition metal complexes. Current projects address the role of Jahn-Teller coupling in determining the structural and magnetic properties of complexes with anisotropic ligands such as water and imidazole. We seek to demonstrate that in order to obtain a satisfactory understanding of metal–water and metal–imidazole interactions, which are central to the functionality of the majority of biological systems, both the electronic and vibrational co-ordinates of the system must be considered.

Keywords: Electronic structure · Transition metal complexes · Vibronic coupling

Selected Projects

Variation of the Effective Magnetic Moment with Temperature [1][2]

Fig. 1 shows the variation of the effective magnetic moment with temperature for Ti(III)-doped $\text{CsGa}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$. Overlaid are two fits to the experimental data. The broken line was calculated by considering the electronic wave-function only and clearly does not provide an adequate description of the experimental data. The solid line gives a much better representation, where Jahn-Teller coupling is included. *This is the first instance in which the effect of Jahn-Teller coupling on the variation of the effective magnetic moment with temperature has been considered.* Our work suggests that even a weak Jahn-Teller interaction can greatly affect the magnetic properties of transition metal complexes and much of the literature needs revising.

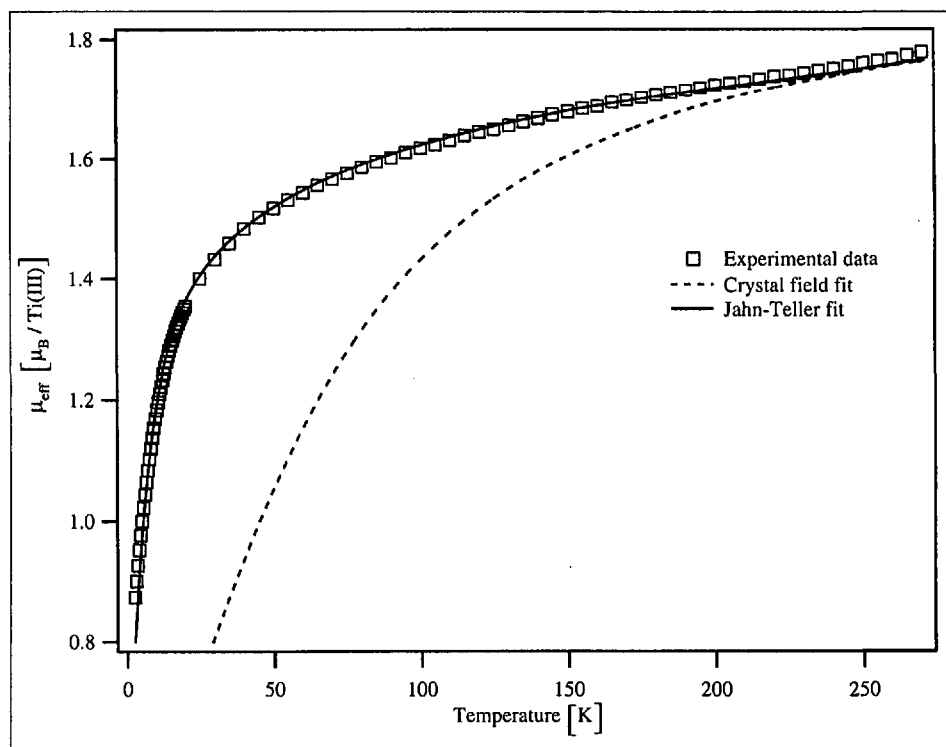


Fig. 1. Variation of the effective magnetic moment of Ti(III)-doped $\text{CsGa}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ with temperature (from [2])

Isotopic Dependence of the EPR Spectrum [2]

The dynamical Jahn-Teller effect can result in significant quenching of spin-orbit coupling and the orbital Zeeman interaction, without introducing magnetic anisotropy. This phenomenon is known

as the Ham effect and arises as a consequence of the reduced overlap of the vibrational parts of the vibronic wave-functions due to the displacement of the potential energy surfaces along the Jahn-Teller active co-ordinates. The Ham effect generally increases as the phonon

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energy decreases, due to the lowering of the zero-point energy. Thus, the quenching of orbital angular momentum by the Jahn-Teller interaction depends strongly on the frequency of the phonon and we have exploited this fact to obtain information regarding the nature of the vibronic interaction. In Fig. 2 are presented EPR data for Ti(III)-doped $\text{CsAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ for three isotopic abundances.

The frequencies of the vibrations of the $[\text{Ti}(\text{OH}_2)_6]^{3+}$ cation have very different dependencies on the isotopic abundance. The EPR spectra presented in Fig. 2 therefore provide direct information concerning the relative Jahn-Teller coupling strengths between the unpaired electron and the vibrations of the $[\text{Ti}(\text{OH}_2)_6]^{3+}$ cation.

Quenching of the Excited State Spin-Orbit Interaction, as Observed by Electronic Raman Spectroscopy [3][4]

In Fig. 3a is shown the Raman spectrum of $[\text{C}(\text{NH}_2)_3][\text{V}(\text{OH}_2)_6](\text{SO}_4)_2$, between 2400 and 3100 cm^{-1} in $y(\text{zy})x$ polarisation geometry.

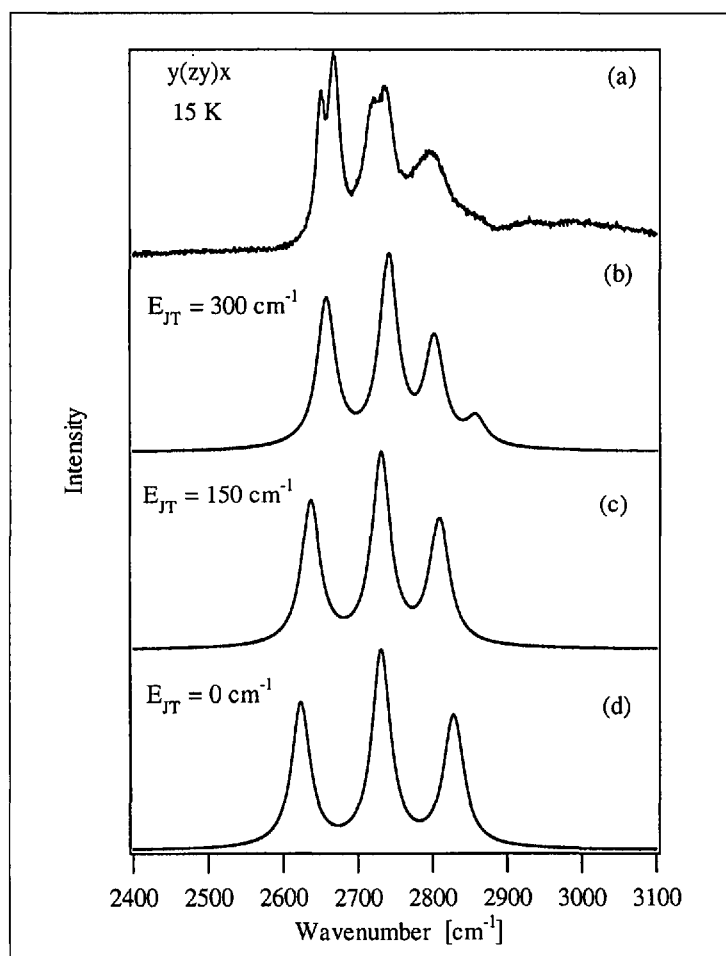


Fig. 3. Single crystal Raman spectrum of $\text{C}(\text{NH}_2)_3[\text{V}(\text{OH}_2)_6](\text{SO}_4)_2$ (from [4]).

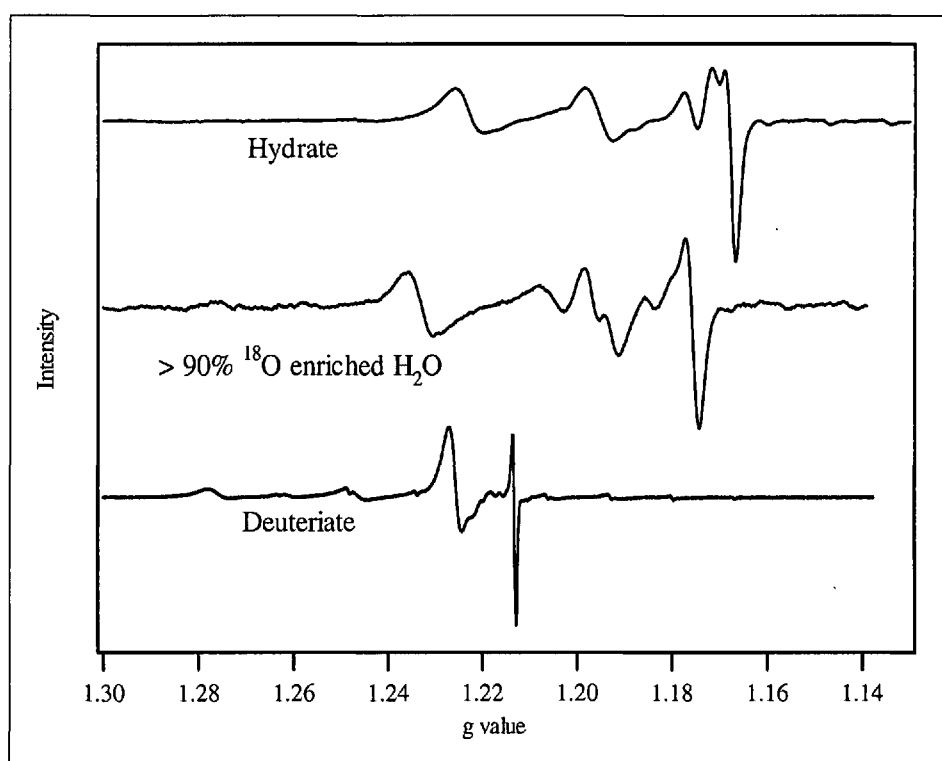


Fig. 2. EPR spectra of Ti(III)-doped $\text{CsAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ for three isotopic abundances. All spectra obtained at ca. 1.7 K with the principal magnetic axis aligned with the field (from [2]).

The Raman bands observed correspond to components of the ${}^3A_g \rightarrow {}^3E_g$ electronic transition of the vanadium(III) cation. Transitions to each of the spinor levels of the 3E_g term of two chemically distinct species are observed. In Fig. 3b–d are displayed calculated electronic Raman profiles for different strengths of Jahn-Teller coupling. As a result of the Jahn-Teller interaction, the potential energy minima of the spinor levels are displaced to differing degrees along the e co-ordinate of the twisting libration of water. This gives rise to a reduction in the spacing between the spinor levels of the 3E term. The electronic Raman spectrum of this system represents one of the clearest examples of the manifestation of the dynamical Jahn-Teller effect.

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