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 CsGa(SO₄)₂·12H₂O. 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 CsGa(SO₄)₂·12H₂O 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
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 CsAl(SO$_4$)$_2$·12H$_2$O for three isotopic abundances.

The frequencies of the vibrations of the [Ti(OH)$_2$]$_6$ 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 [Ti(OH)$_2$]$_6$ 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 [C(NH$_2$)$_3$][V(OH)$_2$]$_6$(SO$_4$)$_2$, between 2400 and 3100 cm$^{-1}$ in $y(zy)x$ polarisation geometry.

The Raman bands observed correspond to components of the $^3$A$_g$ $\rightarrow$ $^3$E$_g$ electronic transition of the vanadium(III) cation. Transitions to each of the spinor levels of the $^3$E$_g$ 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 $^3$E term. The electronic Raman spectrum of this system represents one of the clearest examples of the manifestation of the dynamical Jahn-Teller effect.

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

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

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