SEMICLASSICAL APPROACH TO THE VIBRONIC PROBLEM FOR THE CREUTZ - TAUBE ION

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ABSTRACT. A semiclassical vibronic coupling model for the Creutz - Taube ion is developed. The electronic energy spectrum obtained in quantum-chemical calculations was used to include vibronic effects. The vibronic constants for the states participating in electron delocalisation are first determined from experimental data.

The usual theoretical approach to the description of mixed valency clusters is based on the calculation of electron-vibrational (vibronic) states of the complex. This idea was introduced first by Piepho, Krausz and Schatz (1978), and then developed by other authors. To calculate vibronic states, the electronic energy spectrum and vibrations responsible for an excess electron localisation must be known. For a dimer, the latter is given by the antisymmetric combination of the totally symmetric distortions of the surroundings of the metal ions. It was recently shown (Piepho 1988) that vibrations connected with change of metal-metal distance must be also taken into account.

Figure 1. The structure of the CT ion.

The application of a model to real compounds must allow to find both electronic and vibronic parameters. However, using one source of experimental information (the intervalence transfer band, for example) does not allow us to find all parameters unambiguously. The calculation of vibronic constants from first principles is complicated by the presence of many odd normal vibrations, whereas in the model only one effective mode is taken into account. At the same time the parameters of electronic structure may be found from quantum-chemical calculations. In the present communication, we shall show how this can be done for the Creutz-Taube (CT) ion \([\text{CNH}_3\text{Ru(pyrazine)}\text{Ru(CNH}_3\text{)}]^{5+}\). We shall not calculate the vibronic states but limit ourselves to the semiclassical approximation. This means that using only one adiabatic effective mode can be justified if we consider it as an "interaction mode" (Toyozawa, Inoue 1966).

The structure of the CT ion is shown schematically in Figure 1. In the octahedral environment the ground state is \(1A_1\) for the divalent ruthenium ion and \(2T_{2g}\) for the trivalent one. In the real structure due to the presence of lower symmetry crystal fields, the orbital triplet is split into three orbital singlets that are mixed by the spin-orbit interaction. The electron transfer can take place from the \(1A_1\) state to any of these three states.

The first calculations considering the low symmetry crystal field and spin-orbit interactions in the CT ion were performed by Neuenschwander, Piepho and Schatz (1985). These authors assumed that the vibronic constants for all the three electronic states are the same and equal to that of the \(\text{Ru(CNH}_3\text{)}_{6}^{2+/3+}\) complex and the parameters of the electronic structure were used as adjustable ones to fit the experimental data of the EPR spectra and the intervalence transfer band. This approach results in similar values of the resonance interactions for all three orbital states; however, this conclusion does not agree with the data on the electronic structure. The analysis shows that only one of the three ruthenium orbitals overlaps effectively with the appropriate MO of pyrazine involved in the resonance interaction.

In the one-electron energy level scheme, the \(t_{2g}\) orbitals of the ruthenium ions are split by the tetragonal and rhombic components of the ligand field. The \(d_{yz}\) and \(d_{x^2-y^2}\) orbitals do not overlap with the valent MO of pyrazine and hence are not subject to strong resonance interactions.

![Figure 2. The energy level scheme of the CT ion.](image-url)