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Rankin, Richard; Seddon, Elaine A.; Teuben, Jan H.; Jonkman-Beuker, Anneke H.; Boer, Dirk K.G. de

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**AN EXPERIMENTALLY BASED DESCRIPTION
OF THE GROUND-STATE WAVEFUNCTION FOR TWO WEAKLY COUPLED ELECTRONS
BY PHOTOELECTRON SPECTROSCOPY AND MAGNETIC SUSCEPTIBILITY MEASUREMENTS**

Jennifer C. GREEN, Richard RANKIN, Elaine A. SEDDON
Inorganic Chemistry Laboratory, Oxford OX1 3TN, UK

and

Jan H. TEUBEN, Anneke H. JONKMAN-BEUKER and Dirk K.G. DE BOER
Laboratory of Inorganic Chemistry, University of Groningen, 9747 AG Groningen, The Netherlands

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It is possible to extract values for the transfer energy, t , and the Coulomb interaction, U , in hydrogen-like systems from a combination of photoelectron and magnetic data, as both the form of the photoelectron spectrum and the exchange splitting are determined by these quantities. This procedure is used to evaluate the ground-state wavefunction for the two weakly coupled Ti 3d electrons in $(C_{10}H_8)(C_5H_5)_2Ti_2Cl_2$.

1. Introduction

Satellite structure in the photoelectron spectra of compounds can provide interesting information on the chemical bonding. Whereas the position of the lines reflect the different initial- and final-state energies of the system, the intensities are determined by the square of the projection of the final on the initial state. So, in principle, if a limited basis set is used, both initial- and final-state wavefunctions can be evaluated from photoelectron spectra. This has been achieved for instance in the case of copper dihalides [1]. In this paper we show that a wavefunction for the two weakly coupled titanium 3d electrons in $(C_{10}H_8)(C_5H_5)_2Ti_2Cl_2$ can be determined from the ultraviolet photoelectron spectrum combined with magnetic susceptibility data.

2. Experimental

The compound $(C_{10}H_8)(C_5H_5)_2Ti_2Cl_2$ was prepared as reported by Olthof [2]. The magnetic susceptibility measurements were obtained using the

Faraday method. The UV photoelectron spectrum was measured in the gas phase, using both He-I and He-II radiation, on a Perkin-Elmer PS 16/18 spectrometer fitted with a Helectros lamp. The sample was sublimed continuously during the measurements at 250°C to a pressure of $\approx 10^{-1}$ Torr.

3. Results and discussion

The compound $(C_{10}H_8)(C_5H_5)_2Ti_2Cl_2$ is a binuclear complex with the titanium atoms η -bonded to the two rings of a fulvalene ligand and bridged by two chlorines (see fig. 1). The distance between the two titanium atoms is 3.6 Å [2]. Both titanium atoms are formally in the III oxidation state and may be considered as d^1 ions.

Measurement of the variation of the magnetic susceptibility with temperature gave the results for χ_m , the molar susceptibility, shown in fig. 2. The behaviour shown is characteristic of molecules with a diamagnetic ground state ($S = 0$) and a low-lying, thermally accessible, paramagnetic excited state. For this complex, with two d^1 ions, we expect a triplet ex-

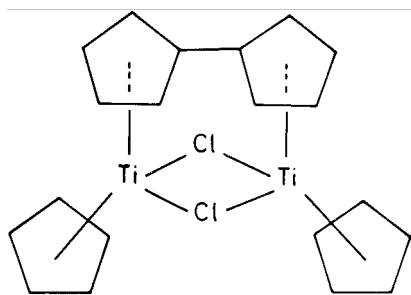


Fig. 1. The structure of $(C_{10}H_8)(C_5H_5)_2Ti_2Cl_2$.

cited state ($S = 1$). The triplet state lies $-2J$ above the singlet ground state: J , the exchange energy, is usually negative. The temperature-dependent part of the susceptibility is given by

$$\chi_T = \frac{Ng^2\mu_B^2S(S+1)}{kT(e^{-2J/kT} + 3)}.$$

The best fit to the experimental data may be obtained with $g = 2$ and $-2J = 750$ K (0.05 eV), and a temperature-independent susceptibility $\chi_0 = -1.6 \times 10^{-4}$ cm^3 $mole^{-1}$.

The photoelectron spectra obtained using both He-I and He-II radiation are shown in fig. 3. The region of d ionization may be readily identified by its

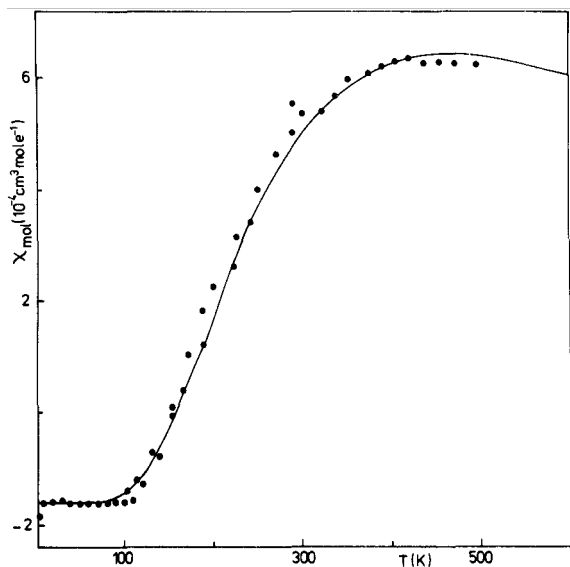


Fig. 2. Variation of the molar susceptibility with temperature. The marks indicate the experimental data. The full curve shows the theoretical fit (see text).

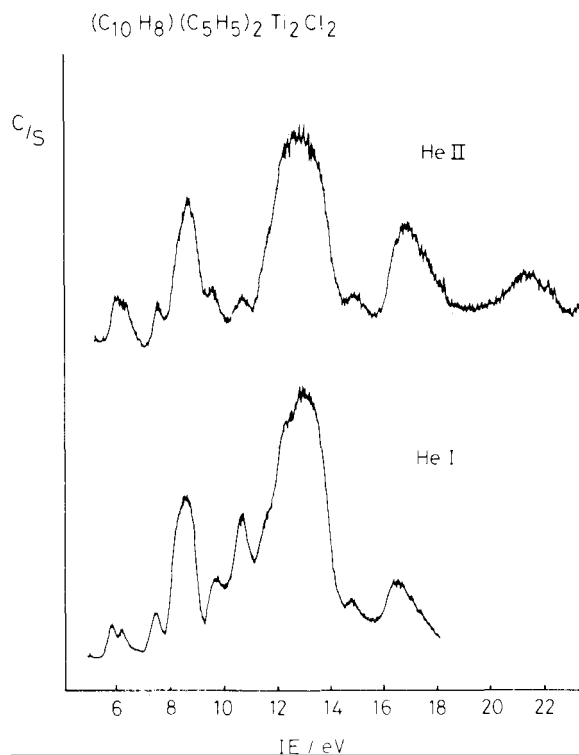


Fig. 3. He-I and He-II photoelectron spectra of $(C_{10}H_8)(C_5H_5)_2Ti_2Cl_2$.

relative intensity increase in the He-II spectrum: it consists of two bands of ionization energy 5.82 and 6.17 eV, the band of lower binding energy having a slightly higher intensity. The occurrence of these two bands cannot be due to the presence of two different initial states for the molecule as the separation between them is too great: at this resolution a broadening of bands will be a consequence of this factor. We may therefore conclude that two final states are accessible on d ionization of this molecule.

If we take a model for the molecule in which we consider just the two d electrons, we have a situation that parallels that of the hydrogen molecule. In the final state, after photoemission, one electron remains as in the hydrogen molecule ion, H_2^+ . The two final states may be identified with the electron in a bonding orbital, ψ_b , or in an antibonding orbital, ψ_a .

The separation of the two final states and the singlet-triplet energy gap are inter-related. In a one-electron model, given A as the wavefunction on atom A and B as the wavefunction on atom B with A and B

orthogonalized, we may define a transfer energy $t = \langle A|h|B \rangle$, where h is the one-electron hamiltonian in the field of the two nuclei. The orbitals for the final state are $\psi_b = 2^{-1/2}(A+B)$ and $\psi_a = 2^{-1/2}(A-B)$.

The energy separation $E_a - E_b$, between the bonding and antibonding levels in the molecular ion, given by $-2t$, is equal to the distance between the two peaks. In the initial state there will be a (partly screened) Coulomb interaction, v_{12} , between the two electrons. If we neglect all two-centre integrals other than the on site Coulomb repulsion integral U , where

$$U = \langle A_1A_2|v_{12}|A_1A_2 \rangle = \langle B_1B_2|v_{12}|B_1B_2 \rangle,$$

the singlet-triplet energy separation is given by $-2J = 4t^2/U$, in the limit of $2|t| \ll U$. There are also singlet states with predominantly two electrons on one atom, that have an energy of $\approx U$ above the ground state.

From our experimental data we obtain the splitting of the two d-bands, $-2t = 0.35$ eV. With the value $-2J = 0.06$ eV, derived from the magnetic susceptibility data, we calculate $U = 2.0$ eV. It is interesting to note that we may expect a weak charge transfer transition at an energy U . In the optical spectrum a band is observed at 533 nm (2.3 eV). However, transitions from Ti to the cyclopentadienyl rings are also expected in this region. The Coulomb integral is considerably reduced as compared with the free ion value, $F^0(3d, 3d) = 17$ eV [3], mainly due to interatomic relaxation.

Whereas the position of photoelectron bands gives the energies of the ionized final states, the intensity pattern is a reflection of the ground-state wavefunction. In a molecular orbital picture, the presence of both final states implies that both the bonding and antibonding orbitals are occupied in the ground-state wavefunction. For the triplet molecules both are equally occupied.

$$\psi_T = 2^{-1/2}[\psi_b(1)\psi_a(2) - \psi_b(2)\psi_a(1)]\phi_T.$$

For the singlet ground state, the relative occupancy depends on the degree of configuration interaction,

$$\psi_S = [c_1\psi_b(1)\psi_b(2) + c_2\psi_a(1)\psi_a(2)]\phi_S.$$

ϕ_T and ϕ_S are the spin wavefunctions for triplet and singlet states.

However, as we are dealing here with a case of weak interactions between electron spins, we prefer to discuss the transition probabilities in terms of a valence

bond description, as in these cases the Heitler-London function is the best first approximation to the wavefunction. The singlet ground state is then described by a function such as

$$\psi_S = \{2^{-1/2}p(A_1B_2 + B_1A_2) - 2^{-1/2}q(A_1A_2 + B_1B_2)\}\phi_S,$$

where $p = \cos \theta$, $q = \sin \theta$, $\theta = \frac{1}{2} \arctg 2x$ and $x = 2t/U$. It is easily verified that $c_1 = (p-q)/2^{1/2}$ and $c_2 = (p+q)/2^{1/2}$. The triplet state is simply

$$\psi_T = \{2^{-1/2}(A_1B_2 - B_1A_2)\}\phi_T.$$

The singlet wavefunction is a mixture of covalent and ionic states; the weighting of the ionic states, which is known as the ionicity, κ , of the valence bond wavefunction, is given by q^2 , and is a function of $2t/U$. When $2t/U$ is small, the ionicity is only $(2t/U)^2$, but when $U \ll |2t|$, $\kappa = 0.5$, and we obtain the molecular orbital wavefunction with both electrons in the bonding level ($c_2 = 0$).

For the experimentally found value of $2t/U = -0.175$, κ has a value of 0.03, so the Heitler-London formula is a good approximation to the ground-state wavefunction.

To calculate the intensities of the two bands we will assume the probabilities of ejecting an electron from ψ_a and ψ_b to be equal. This corresponds to neglecting interference terms. For randomly oriented diatomic molecules in which the atomic orbitals have a small spatial extension in comparison to the size R of the molecule, the interference terms is $(\sin kR)/kR$, k being the wave number of the continuum electron in the final state. The effect of this term is only small when $kR \geq 2\pi$, which condition is fulfilled in our case. If I_a is the intensity of the band where the electron is left in the antibonding orbital ψ_a and I_b is the intensity of the band where the electron is left in the bonding orbital ψ_b , the ratio for photoemission from singlet molecules is given by

$$I_a^S/I_b^S = [(p+q)/(p-q)]^2.$$

When $x = 2t/U$ is small

$$I_a^S/I_b^S \approx (1+2x)/(1-2x).$$

When $|x|$ is large ($U \ll |2t|$) we obtain $I_a/I_b \approx 0$; in this case the molecular orbital description of the ground state is valid ($c_2 = 0$), and only one band will

be observed in the photoelectron spectrum.

For the triplet molecules

$$I_a^T/I_b^T = 1.$$

The experimental band intensity ratio will depend on the fraction of molecules in the triplet and singlet states (n_T and n_S respectively)

$$I_a/I_b = (n_T I_a^T + n_S I_a^S)/(n_T I_b^T + n_S I_b^S),$$

$$n_T = 3/(e^{-2J/kT} + 3), \quad n_T + n_S = 1.$$

At the temperature of the experiment (520 K) we calculate $n_T = 0.44$ and $n_S = 0.56$.

Using this value we may predict the intensity ratio of the photoelectron bands. For values of 0.175 for $2t/U$ and 0.44 for n_T , we obtain $I_a/I_b = 0.66$. This is in good agreement with the experimentally observed ratio of peak heights which is ≈ 0.7 .

It is in principle possible to extract t and U from the observed splitting and intensity ratio in the photoelectron spectrum on its own. However, because of the experimental uncertainty in the intensities, the procedure is less accurate than the one that we have employed.

The observed transfer energy is rather small. It should be noted that it is not possible to conclude whether the transfer occurs directly or via a bridge. In the case of transfer via a bridge we have to consider the transfer energy b between metal and ligand, and the energy separation Δ between the metal and ligand levels. We will neglect the Coulomb interaction of two electrons on the ligand. If $b \lesssim U \ll \Delta + U$ we may take $t \approx b^2/(\Delta + U)$ as an effective transfer energy between the two metal ions. Then our preceding contemplations are still true. The fulvalene π -orbitals

have $\Delta \approx 2.5$ eV. For that value our approximation results in an overestimate of U . A more elaborate calculation shows that the obtained U will be reduced by $\approx 30\%$. Furthermore, the intensity I_b will be changed, because the bonding function now gets some ligand character. However, this effect is only small if the ligand photoionization cross section does not exceed five times the metal cross section.

In conclusion we have shown that from a combination of magnetic susceptibility and photoelectron measurements, it is possible to obtain important information on binuclear compounds, like the ionicity (κ), the on site Coulomb interaction (U) and the transfer integral (t). For $(C_{10}H_8)(C_5H_5)_2Ti_2Cl_2$ we find $\kappa = 0.03$, $U = 2.0$ eV and $|2t| = 0.35$ eV.

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