

## Electron attachment to $\text{TiCl}_4$

J A Tossell, J H Moore and J K Olthoff†

Department of Chemistry, University of Maryland, College Park, MD 20742, USA

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**Abstract.** The derivative electron transmission spectrum is presented for gaseous  $\text{TiCl}_4$  between 0 and 10 eV. The spectral features are consistent with a high scattering cross section just above threshold and with a weak shoulder in the cross section around 6 eV. Multiple-scattering  $X_\alpha$  molecular orbital calculations establish that addition of an electron to the e or  $t_2$  crystal field orbital gives a stable anion. Calculated vertical electron affinities for these orbitals are in good agreement with experimental values from studies of donor-acceptor complexes. Addition of an electron to any of the higher-energy  $\sigma^*$  orbitals is calculated to yield an unstable negative ion. Multiple-scattering  $X_\alpha$  continuum calculations show very large elastic scattering cross sections just above threshold, near the energies calculated for these  $\sigma^*$  orbitals. The calculated cross section shows a weak local maximum at about 7 eV. Correspondences are drawn between the high stability of the crystal-field orbital-occupied anions and the high ultraviolet and x-ray term energies of these orbitals.

### 1. Introduction

$\text{TiCl}_4$  has been extensively studied, both experimentally (Bancroft *et al* 1982) and theoretically (Gupta and Tossell 1982, Tse 1981, Tossell 1979), because it is a tetrahedral  $d^0$  transition-metal complex which is volatile, readily available and reasonably easy to handle. Most spectral studies on  $\text{TiCl}_4$  have used photons, either to create excited states of the neutral molecule or to form cations by photoemission. The energies of orbitals occupied in the ground state have been completely determined and energies for excitation of Cl 3p electrons to the empty e and  $t_2$  crystal-field orbitals have been accurately determined (Gupta and Tossell 1982, Tse 1981, Tossell 1979, Becker *et al* 1969). It is now well established that the core photoemission spectra of  $\text{TiCl}_4$  show satellites which correspond qualitatively to 'Cl 3p  $\rightarrow$  Ti 3d charge transfer' although these satellite energies differ systematically from their optical analogues due to different selection rules and perturbation of the orbitals by the presence of the core holes (Gupta and Tossell 1982, Tse 1981, Tossell 1979). The  $t_2$  symmetry 'crystal-field orbital' also yields a feature in the x-ray absorption near-edge spectrum (XANES) which lies well below the absorption edge.

By contrast, little is known about the interaction of  $\text{TiCl}_4$  with electrons. Studies of the absorption spectra of donor-acceptor complexes of  $\text{TiCl}_4$  (in solution) have yielded vertical electron affinities which should correspond to energies for addition of electrons to the crystal-field orbitals (Hatano and Ito 1971).

† Present address: Pharmacology Department, The Johns Hopkins School of Medicine, Baltimore, MD 21205, USA.

We present here the electron transmission spectrum (ETS) obtained by passing a low-energy monochromatic electron beam through a gaseous  $\text{TiCl}_4$  sample (Jordan and Burrow 1978). The quantity measured is the variation of the transmitted electron current with electron energy. The transmitted current varies inversely with the total electron scattering cross section. The experiment is generally run in the energy derivative mode (Sanche and Schulz 1972). From the derivative spectrum we have generated the relative cross section as a function of energy.

## 2. Results

The derivative electron transmission spectrum of  $\text{TiCl}_4$  is shown in figure 1. The relative total cross section over the range 2.5–9.0 eV is shown in the inset. This was obtained by digitising the derivative spectrum. Since we have no calibration for the absolute cross section or the value of the derivative we can calculate only the qualitative shape of the experimental total cross section. There are ETS features corresponding to fluctuations in the rate of change of the local cross section at about 3.6, 5.8 and 8.2 eV and near threshold there is a broadening of the current spike arising from abrupt turn-on of the electron beam. Thus, electron attachment processes or large fluctuations in cross section also occur near threshold. In figure 2 we show the elastic electron scattering cross section calculated for the  $\text{TiCl}_4$  using the previously described multiple-scattering  $X\alpha$  (ms  $X\alpha$ ) method (Tossell and Davenport 1984, Davenport *et al* 1978). The potential for this scattering calculation was obtained self-consistently for the  $5t_2 \sigma^*$  orbital electron attachment transition state, i.e. for 0.5 electrons in this  $t_2$  orbital. Since the eigenvalue for this orbital in the transition state was positive, we used a charge-sphere stabilisation technique in the self-consistent field (SCF) process but its effect on the potential was later subtracted out (Tossell and Davenport 1984). Using the bound-state ms  $X\alpha$  method we first established that the e and  $t_2$  crystal-field states

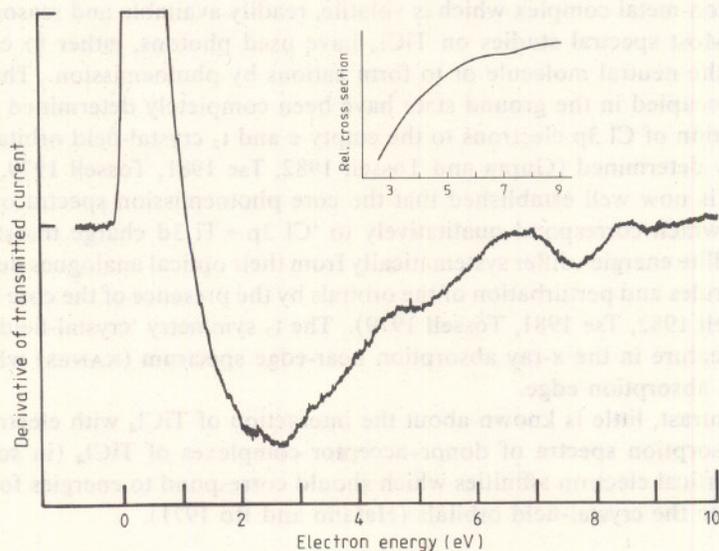


Figure 1. Derivative electron transmission spectrum of  $\text{TiCl}_4$  and relative total cross section (inset).

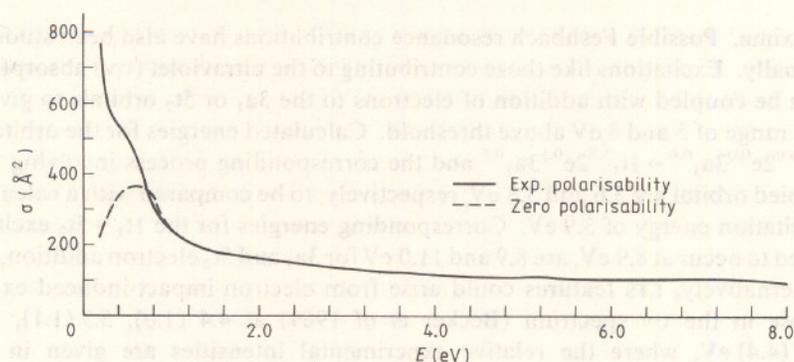


Figure 2. Continuum MS  $X\alpha$  elastic electron scattering cross sections for  $\text{TiCl}_4$ : — total ( $a_1+t_2+e+t_1$ ).

( $2e$  and  $4t_2$  in the usual numbering scheme) gave stable negative ions. The calculated vertical electron affinity (EA) of 2.9 eV for the  $2e$  orbital compares fortuitously well with the experimental value of 2.87 eV (Hatano and Ito 1971), as shown in table 1. The relevant transition state for calculation of elastic scattering cross sections must therefore be some higher-energy state and we have selected the  $5t_2$  state, of Ti-Cl  $\sigma^*$  character, as representative of states in this energy range. This potential was matched to a polarisation potential at large distance obtained using the experimental static electric dipole polarisability (Verma and Pandey 1978). The partial-wave basis was limited to  $l_{\max} \leq 5$  for the outer sphere and the Ti and to  $l_{\max} \leq 1$  for the Cl. The calculated cross sections in the  $a_1$  and  $t_2$  channels are very large near threshold with the  $t_2$  cross section showing a maximum at about 0.1 eV when the experimental polarisability is used. If the polarisation potential is set to zero the threshold cross sections are greatly reduced, as shown in figure 2. The stabilised bound-state calculation gives an attachment energy of 0.7 eV for the  $5t_2$  orbital, reasonably close to the  $t_2$  cross section maximum, while the calculated attachment energy for the  $3a_1$  is -0.2 eV, i.e. it is a stable anion. There is also a much weaker local maximum in the calculated total elastic cross section at about 7 eV, arising mainly from the  $t_2$  channel.

It thus appears that the crystal-field orbitals of  $\text{TiCl}_4$  do not contribute to the ETS, that the Ti-Cl  $\sigma^*$  orbitals contribute only to the very near-threshold region and that only some of the derivative ETS features correspond to elastic scattering cross section

Table 1. Calculated and experimental values for energetics (in eV) of  $2e$  and  $4t_2$  crystal-field orbitals of  $\text{TiCl}_4$ .

	2e orbital		4t <sub>2</sub> orbital	
	Calc.	Exp.	Calc.	Exp.
Vertical electron affinity	2.9	2.87 <sup>a</sup>	1.9	—
Ultraviolet excitation energy, $1t_1 \rightarrow 4t_2$	3.8	4.4 <sup>b</sup>	4.9	5.4 <sup>b</sup>
X-ray absorption spectrum term energy			10.8	—

<sup>a</sup> Hatano and Ito (1971).

<sup>b</sup> Becker *et al* (1969).

maxima. Possible Feshbach resonance contributions have also been studied computationally. Excitations like those contributing to the ultraviolet (UV) absorption spectrum can be coupled with addition of electrons to the  $3a_1$  or  $5t_2$  orbitals to give energies in the range of 5 and 8 eV above threshold. Calculated energies for the orbital excitations  $1t_1^{6.0}2e^{0.0}3a_1^{0.0} \rightarrow 1t_1^{5.5}2e^{0.5}3a_1^{0.5}$  and the corresponding process involving the  $5t_2$  unoccupied orbital are 3.6 and 3.8 eV, respectively, to be compared with a calculated  $1t_1 \rightarrow 2e$  excitation energy of 3.9 eV. Corresponding energies for the  $1t_1 \rightarrow 5t_2$  excitation, calculated to occur at 8.9 eV, are 8.9 and 11.0 eV for  $3a_1$  and  $5t_2$  electron addition, respectively. Alternatively, ETS features could arise from electron-impact-induced excitations like those in the UV spectrum (Becker *et al* 1969) at 4.4 (1.0), 5.3 (1.1), 7.3 (3.5) and 9.3 (4.4) eV, where the relative experimental intensities are given in parentheses. However, such Feshbach resonances and excitations would give very narrow ETS features. No features consistent with Feshbach resonances or inelastic excitations occur in the range 2.5–9.0 eV shown in the inset of figure 1.

### 3. Discussion

The stability of negative ions arising from electron capture into the  $2e$  and  $4t_2$  orbitals is consistent with observed UV photoemission (Bancroft *et al* 1982) and UV absorption (Becker *et al* 1969) data. Using the transition-state approach (Slater 1972) we can relate the  $1t_1$  orbital ionisation potential (IP), the  $1t_1 \rightarrow 2e$  orbital excitation energy and the  $2e$  orbital electron affinity as shown in figure 3. The  $1t_1$  IP and  $1t_1 \rightarrow 2e$  excitation energy are directly available from experiment and can also be obtained from eigenvalues or eigenvalue differences in the self-consistent transition state, with orbital occupation numbers halfway between those of the initial and final states. The large x-ray term energy of 10.8 eV (table 1) calculated for the  $2e$  orbital (where the term energy is the Ti  $1s$  IP minus the Ti  $1s \rightarrow 2e$  excitation energy, both from transition-state calculations) is also consistent with high stability for the  $2e$  orbital. Unfortunately, although the Ti K x-ray absorption spectrum of  $TiCl_4$  is available (Gregor *et al* 1983), the Ti  $1s$  IP has not been determined directly. However, the Ti  $1s$  IP can be estimated from Ti  $3p$  IP for  $TiCl_4(g)$  of 44.6 eV (Mousty-Desbuquoit *et al* 1983) and the Ti  $K\beta$  (Ti  $3p \rightarrow Ti$ ) x-ray emission energy of 4931.6 eV (Koster and Mendel 1970) in  $TiO_2$  to be about 4976 eV. The XANES of  $TiCl_4(g)$  shows a feature attributable to a Ti  $1s \rightarrow 4t_2$  excitation

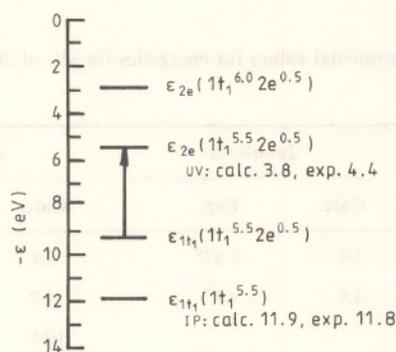


Figure 3. Relationship between  $1t_1$  IP,  $1t_1 \rightarrow 2e$  excitation energy and electron affinity of  $2e$  orbitals using transition-state model.

at 4967.2 eV (Greegor *et al* 1983), indicating a term energy of about 9 eV, in reasonable agreement with the calculated value of 10.8 eV.

Further work on this molecule should involve direct studies of the total absolute cross section (in a non-derivative mode), and continuum  $ms X\alpha$  calculations utilising larger partial-wave bases, refinements in the treatment of exchange, etc. Nonetheless, it is clear that the Ti 3d crystal-field orbital-derived anions are stable and so do not contribute to the ETS and that the  $a_1$  and  $t_2$  symmetry Ti-Cl  $\sigma^*$  orbital-derived anions lie very close to threshold and contribute to the large cross sections calculated just above threshold. The shoulder at about 6 eV in the simulated total cross section probably arises from a broad feature calculated at about 7 eV in the elastic cross section but contributions from inelastic processes cannot completely be ruled out.

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