# Photoelectron Spectra and Bonding of Covalent Metal Nitrates

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Summary　He II photoelectron spectral data for $Ti(NO_3)_4(g)$ and $Cu(NO_3)_2(g)$ are interpreted with the aid of ab initio molecular orbital calculations and show that the metal ligand bonding involves those orbitals which correlate with the $4e'$ m.o.'s of the ligands; the ionization energies are consistent with the nitrato-groups of $Ti(NO_3)_4(g)$ having a smaller overall negative charge than those of $Cu(NO_3)_2(g)$.

THE simple, covalent, anhydrous metal nitrates are well characterised[1] and typically exhibit remarkable reactivities. However, no photoelectron (p.e.) spectral data have been reported and no experimentally confirmed description of their electronic structure has been presented. Therefore, we have undertaken such a study and herein we report and interpret the He II p.e. spectra of $Ti(NO_3)_4(g)$ and $Cu(NO_3)_2(g)$.

$Ti(NO_3)_4(g)$[2] and $Cu(NO_3)_2(g)$[3] comprise discrete molecular species with symmetrically bidentate nitrato-groups. He II p.e. spectra were recorded for samples sublimed at ca. 24 and 150 °C, respectively. These are shown in Figures 1 and 2, together with the relative ionization potentials for the nitrate ion taken from the p.e. spectrum recorded[4] for $CsNO_3$.

The formal $d^0$ configuration of the metal atom in $Ti(NO_3)_4$ means that all the molecular orbitals (m.o.'s) of this molecule correlate with those of the free ligand, as shown earlier by an ab initio SCF–MO calculation for this complex.[5] This calculation (see Table 1, ref. 5) provides a satisfactory basis for the interpretation of the $Ti(NO_3)_4$ spectrum and the detailed correlations are shown in Figure 1. The
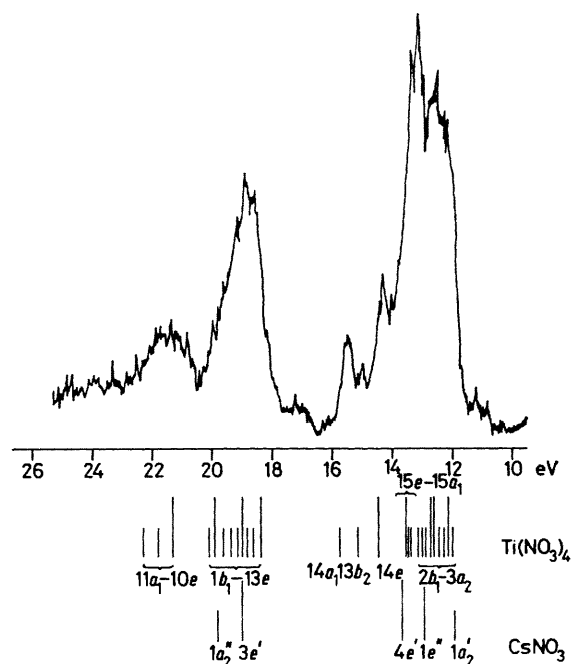


FIGURE 1.　He II p.e. spectrum of $Ti(NO_3)_4(g)$.

lowest energy feature of the spectrum is assigned to ionizations from the orbitals $3a_2$—$2b_1$, having a calculated energy spread of 1·7 eV,[5] which correlate with the $1a_2'$ (oxygen $2p_\sigma$) and $1e''$ (oxygen $2p_\pi$) orbitals of the nitrate ligand.

The second, sharper, spectral feature is assigned to the $15a_1$—$15e$ m.o.'s which correlate with the $4e'$ (oxygen $2p_\sigma$) m.o.'s of the nitrate anion. The calculated spread of these orbital energies (0·2 eV) is consistent with the relative sharpness of this peak. The next three weaker features are assigned to the $14e$, $13b_2$, and $14a_1$ m.o.'s, respectively, which also correlate with the $4e'$ orbitals of the nitrate groups, but have significant titanium $3d$ and $4s$ character and contribute to the metal–ligand bonding interactions. The next major feature of the spectrum, which shows marked asymmetry to higher binding energy, is attributed to ionizations from the $13e$—$1b_1$ m.o.'s, their calculated energy spread being 2·1 eV. These orbitals correlate with the $3e'$ (N–O $\sigma$-bonding) and $1a_2''$ (N–O $\pi$-bonding) orbitals of the ligands. The final feature of the spectrum is attributed to ionizations from the $10e$—$11a_1$ m.o.'s, having a calculated energy spread of 1·0 eV, which correlate with the $4a_1'$ (N–O $\sigma$-bonding) m.o. of the nitrate groups.
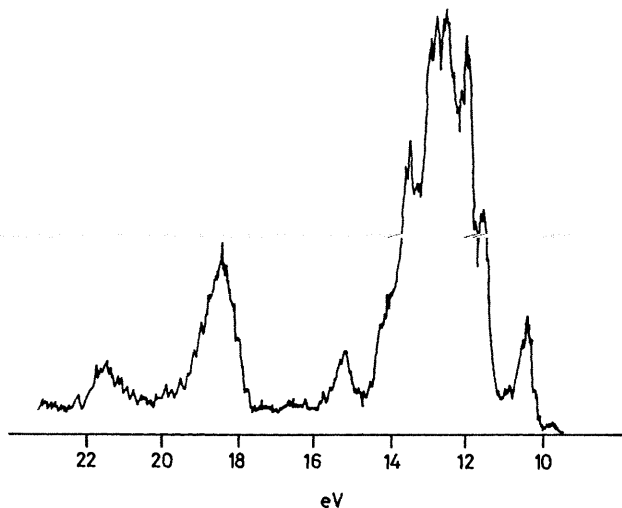


FIGURE 2. He II p.e. spectrum of $Cu(NO_3)_2(g)$.

The He II p.e. spectrum of $Cu(NO_3)_2(g)$ has a profile broadly similar to that of $Ti(NO_3)_4(g)$, except that two additional features are apparent to lower binding energy and the intensity of the complex band centred at 12·5 eV, relative to the band at ca. 18·5 eV is greater in the spectrum of the copper compound than in the spectrum of the titanium compound. Differences in the low ionization energy region are expected owing to the presence of the nine metal '$d$' electrons in $Cu(NO_3)_2$ and the differing interactions between the nitrate ligands in $Cu(NO_3)_2$ and $Ti(NO_3)_4$. An ab initio SCF–MO calculation has confirmed that, apart from the low energy features, the interpretation of the $Cu(NO_3)_2$ spectrum follows that for $Ti(NO_3)_4$. The lowest energy feature is assigned to the ionic states ($^3A_2$, $^1A_1$, $^1B_1$, $^1B_2$) arising from the partially occupied $e$ m.o.'s of mainly copper $3d$ character. The shoulder at 11·65 eV, on the lower energy side of the principal spectral feature, is attributed to some of the ionizations from the metals $a_1$, $b_1$, and $b_2$ $d$ orbitals. These give rise to six ion states, three $^3E$ and three $^1E$. The remainder overlap the ligand ionizations and are responsible for the increased intensity of this complex band.

Thus, these p.e. spectra provide a clear description of the electronic structure of these covalent nitrato-complexes. The metal–ligand bonding interactions are seen predominantly to arise from the $4e'$ m.o.'s of the ligands, in agreement with earlier theoretical predictions.[5] The shift of the ionization energy (i.e.) for the feature which correlates with the $3e'$ and $1a_2''$ N–O bonding orbitals from 18·8 eV for $Ti(NO_3)_4(g)$ to 18·5 eV for $Cu(NO_3)_2(g)$, is consistent with the nitrato-groups of the former having a smaller overall negative charge than those of the latter [cf. the corresponding i.e. for $CsNO_3(g)$ of ca. 16·0 eV[4]]. The ab initio calculations estimate the formal overall charge on the nitrate group to be $-0.53e$ for $Ti(NO_3)_4(g)$ and $-0.69e$ for $Cu(NO_3)_2(g)$. This difference in ligand charge distribution presumably arises from the greater number of $d$ orbitals, into which L→M electron donation can occur, for the titanium(IV) complex as compared to the copper(II) complex.

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