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Core-Level Satellites in the X-ray Photo-Electron Spectra of Tetra-cyanoquinodimethane and its Metal Salts

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Core-Level Satellites in the X-ray Photo-Electron Spectra of Tetracyanoquinodimethane and its Metal Salts

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Abstract—Core-level splittings (C_{1S} and N_{1S}) of between 2 and 3 eV occur in a wide range of anion radical salts of tetracyanoquinodimethane (TCNQ) and also in the parent material. It is suggested that the satellites are associated with the multiple configurations which contribute to the ground-state wave function of these molecules.

Resumé—Un dédoublement des raies des électrons internes (de C_{1S} et N_{1S}) de 2 à 3 eV est mis en évidence pour le tétracyanoquinodiméthane (TCNQ) et un grand nombre de sels où celui-ci est un radical anionique.

On suggère que les satellites sont associés à la configuration multiple qui contribue à la fonction d'onde de l'état initial de ces molécules.

In addition to the well-known dependence of the binding energy of core electrons upon chemical environment (ESCA chemical shifts) other types of core-level splitting have been experimentally identified. Exchange interaction accounts for satellites in the core-levels of both transition-metal compounds and of gaseous paramagnetic species, and the complex spectra displayed by certain heavy-element compounds are broadly interpretable in terms of electrostatic interactions.(1) Other mechanisms may, however, give rise to the observation of satellites in high energy photoelectron spectra. Thus, interaction amongst ionic configurations may lead to the observation of ionic states by an intensity borrowing mechanism, in which the major component involves ionization together with excitation of a valence electron.$^{(2-4)}$ Satellite peaks observed in the spectra of transition-metal carbonyls lead to another possible explanation of such phenomena.$^{(5)}$ Thus, if the molecular ground state is poorly described by a single determinantal function in the Hartree–Fock limit, then transitions to ionic states which correlate with the various configurations of the ground state may be observed.

In this communication we report experimental observations of satellites in 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) and a few of its salts. TCNQ readily forms anion radical salts with simple metallic cations:$^{(6)}$ the stoichiometry for the alkali elements$^{(7)}$ is M TCNQ, but caesium also forms the Cs_2 $(TCNQ)_3$ compound,$^{(8)}$ in which it is thought two TCNQ species bear a (delocalized) charge and the other is neutral.

High resolution spectra of the solid samples of the various TCNQ salts were recorded using an AEI ES100 spectrometer (Al $K\alpha_1\alpha_2$ radiation—1486.6 eV—being chiefly used). To allow for charging effects, and thereby to arrive at absolute binding energies, repeat spectra were recorded on samples which had evaporated on to their surfaces, microcrystallites of gold, the $4f_{5/2}/4f_{7/2}$ spin doublet of which, taking the binding energy values quoted by Siegbahn, could be used as a calibrating reference (see Ref. 9 for full details).

Figure 1 shows relevant regions of a typical scan for a TCNQ salt. The C_{1s} peak, as expected from the different chemical environments

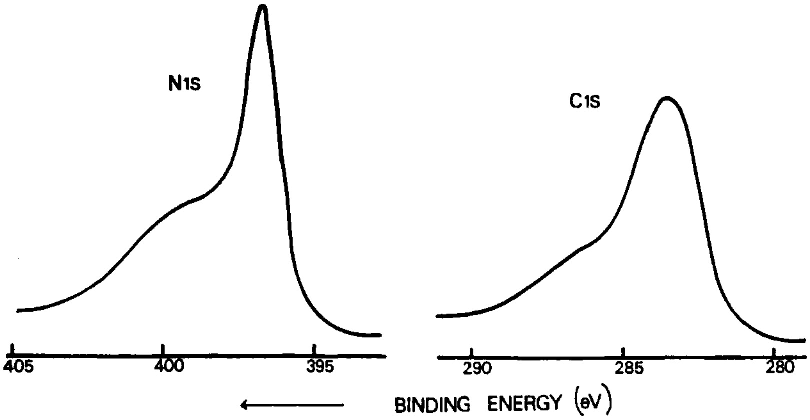

Figure 1. Typical appearance of C_{1s} and N_{1s} peaks in metal TCNQ anion radical salts. Both curves refer to Li TCNQ.

of the carbon in the structure, is rather broad, the FWHM being 2.7 eV for the Li compound, with a corresponding value for graphite of 1.25 eV. But the N_{1s} peak is predictably sharper (FWHM = 1.4), there being crystallographic proof of the near equivalence of all the nitrogen atoms in the salts of the type M TCNQ and in the parent material. It is to be noted that satellite peaks are present on the high binding energy side of both the carbon and the nitrogen core levels. To extract the appropriate quantitative data we have concentrated on deconvoluting only the main and satellite N_{1s} peaks (see Fig. 2). For the series Li TCNQ, Na TCNQ, K TCNQ, Cs TCQN and Cs_2 $TCNQ_3$ the extent of splitting is in the range 2.3 ± 0.4 eV, and the satellite to main peak intensity (computed from the areas) varies from 0.3 : 1.0 to 1.8 : 1.0. TCNQ itself (recrystallized from acetonitrile solution or multiply sublimed) also displays the splitting.

Although there can be no doubt about the reality of the splitting, its origin is, as yet, imperfectly understood. It is tempting to interpret the satellite peaks as arising from a two-electron process, where the emission of a 1s electron (from nitrogen or carbon) is accompanied by an excitation of a valence electron to a vacant band in the solid, or to a $\pi \rightarrow \pi^*$ transition. PPP-calculations on $TCNQ^0$ and $TCNQ^-$ (as free molecules) do in fact reveal that transitions from the highest occupied molecular orbitals to unoccupied M.O's involve energies

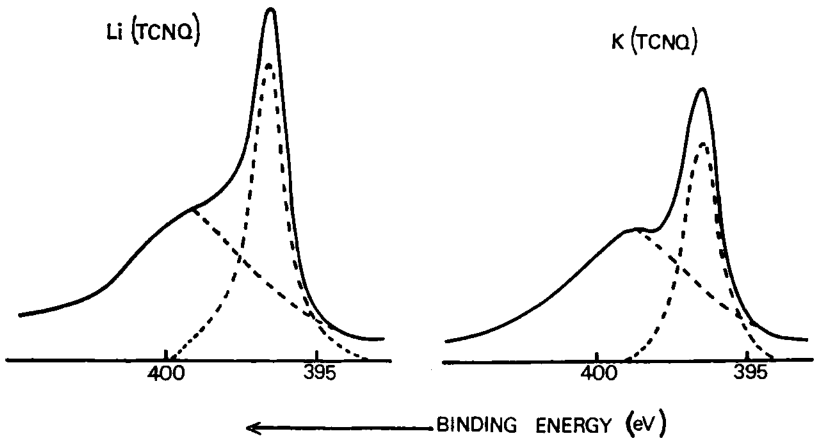

Figure 2. Illustration of deconvoluted N_{1s} peaks.

of 2 to 3 eV (2.8 eV for $TCNQ^0$ and 1.2 and 2.9 eV for $TCNQ^-$). However, if this were the real origin of the satellites we should also expect pronounced satellite structures in the core level peaks of other π-conjugated molecules. Although there is indeed some slight asymmetry in the C_{1s} peaks of a range of aromatic hydrocarbons(10) (pyrene, perylene, chrysene, coronene and even graphite), the effect is so small in these materials as to render this interpretation unlikely.

It is thus possible, that, as with the carbonyls mentioned earlier, the TCNQ salts and the parent material have ground states inadequately described in the Hartree–Fock limit and that the satellites arise essentially because there are at least two major configurations in the ground state. Preliminary results on some other charge transfer systems, notably the graphite intercalates,(11) reveal that satellite peaks similar to those reported here may be a widely occurring phenomenon.

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