109. The Photoelectron Spectrum of Tetracyanomethane[1])

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(11. II. 76)

Summary. The helium (I) photoelectron spectrum of $C(CN)_4$ curiously displays ionizations only in two small windows from 13.8 eV to 14.5 eV and from 14.8 eV to 15.5 eV, respectively. A tentative assignment of the numerous overlapping bands – based on a spectroscopically parametrized LCBO MO model – correlates satisfactorily with ionization potentials of other cyano compounds as well as of tetrahalomethanes.

Tetracyanomethane [2], a tetrahedral molecule [3] [4] of unusual reactivity, *e.g.* [2]

$$C(CN)_4 + LiCl \rightarrow LiC(CN)_3 + ClCN \qquad (1)$$

exhibits in spite of its total 40 valence electrons only two adjacent multicomponent band systems within the helium(I) spectral region (Fig. 1).

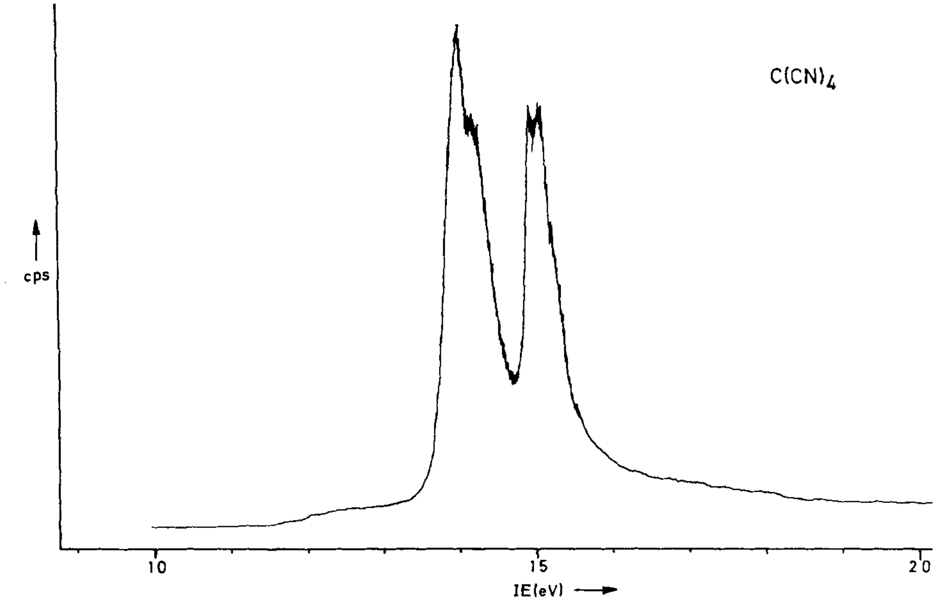

Fig. 1. *He(I) PE. spectrum of $C(CN)_4$*

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Especially for cyano compounds, even *ab initio* SCF calculations fail to reproduce – via *Koopmans'* theorem – PE. band sequences corresponding to closely packed radical cation states [5] [6]. Therefore, the assignment of the $C(CN)_4$ He(I) PE. spectrum is attempted by a bond orbital model, parametrized with observed ionization potentials [7] (Fig. 2).

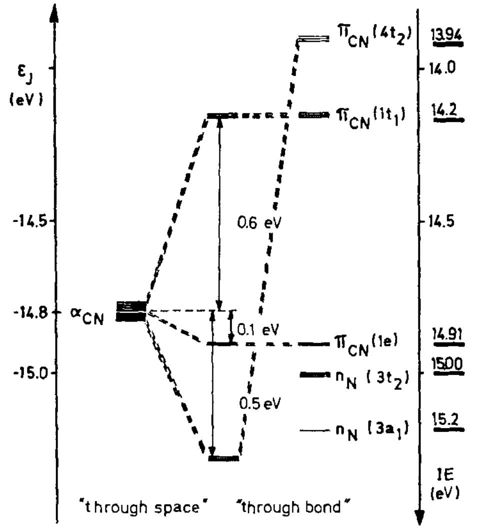

Fig. 2. *MO-diagram for $C(CN)_4$, obtained from interaction of bond orbitals*

The set of 20 occupied valence molecular orbitals, belonging to the T_d irreducible representations $\Gamma = 3a_1 + 1e + 1t_1 + 4t_2$ can be denoted according to their predominant contributions as follows: $\pi_{CN}(t_1 + t_2 + e)$, $n_N(t_2 + a_1)$, and $\sigma_{CN}(t_2 + a_1)$. Judging from the detailed PE. spectroscopic discussion of dicyanomethane $H_2C(CN)_2$ [7] with assigned ionization potentials $\pi_{CN} = 12.7$ eV to 14.2 eV, $n_N = 13.4$ eV and 13.6 eV as well as $\sigma \geqslant 17.3$ eV, only ionizations π_{CN} and n_N are expected within the 13.9 eV to 15.2 eV region of the tetracyano-derivative (Fig. 1). Assuming in addition that *Jahn-Teller* distortions can be neglected as proposed *e.g.* for the π_{CN} ionizations of H_3CCN [8] or for the n_X bands of tetrahalomethanes [9–11], the following arguments lead to the splitting scheme (Fig. 2): (*1*) The π_{CN} orbitals $1t_1$ and 1e, singled out by symmetry, are not affected by 'through bond' interactions. Their separation due to 'through space' interaction can be approximated by substituting the PE. parameters for dicyanomethane [7]

$$\beta_\sigma^{CN} = \frac{-\Delta\pi_\sigma}{2} = -0.5\ \text{eV}\ , \quad \beta_\pi^{CN} = \frac{-\Delta\pi_\pi}{2} = -0.25\ \text{eV} \tag{2}$$

into the equations calculated for lone pair splitting in CX_4 molecules [11].

$$\Delta\text{IP} = \text{IP}(^2\text{E}) - \text{IP}(^2\text{T}_1) = -\frac{1}{2}(\beta_\sigma - \beta_\pi) - \frac{1}{2}(\beta_\sigma + 3\beta_\pi) = 0.75\ \text{eV}. \tag{3}$$

(*2*) The only ionization energy difference of about this size in the PE. spectrum of $C(CN)_4$, *i.e.* $IE_3 - IE_2 = 14.91$ eV $- 14.2$ eV $= 0.71$ eV, consequently suggests the assignment $\pi_{CN}(1t_1)$ for IE_2 and $\pi_{CN}(1e)$ for IE_3. (*3*) This partial assignment in return yields [11] the center of gravity parameter $\alpha_{CN} = -14.8$ eV, more negative than the ones derived for tetracyano-ethylene [6] and for carbonyl cyanide [12] (4). Therefore, the n_N ionization energies should also be increased, and accordingly $n_N(3t_2)$ is attributed to $IE_4 = 15.0$ eV and $n_N(3a_1)$ to $IE_5 = 15.2$ eV. (*4*) The remaining orbital $\pi_{CN}(4t_2)$ must correspond to $IE_1 = 13.94$ eV. Its considerable shift of more than 1.3 eV can be rationalized within the LCBO MO model by strong 'through bond' interactions with both of the lower $\sigma(2t_2)$ and $n_N(3t_2)$ orbitals.

The above assignment not only is in accord with the relative band intensities and with the expected large separation between the two $^2T_2$ cation states, but also fits into a correlation of PE. spectroscopic observations for cyano-derivatives, *e.g.*

	H_3CCN	$H_2C(CN)_2$	TCNE	$OC(CN)_2$	$C(CN)_4$	
α_{CN}	-13.2	-14.1	-14.5	-14.6	-14.8 eV	(4)
$IE(n_N)$	13.1	13.4 13.6	14.0 ± 0.2	14.3 14.4	15.0 eV 15.2 eV	

The values (4) clearly demonstrate, that increasing cyano substitution at one center lowers the π_{CN} center of gravity and raises the n_N ionization energies. A comparison of the π_{CN} ionizations with the n_X ionizations of tetrahalomethanes (Fig. 3) shows, that the pseudo halide $C(CN)_4$ occupies a position between CF_4 and CCl_4.

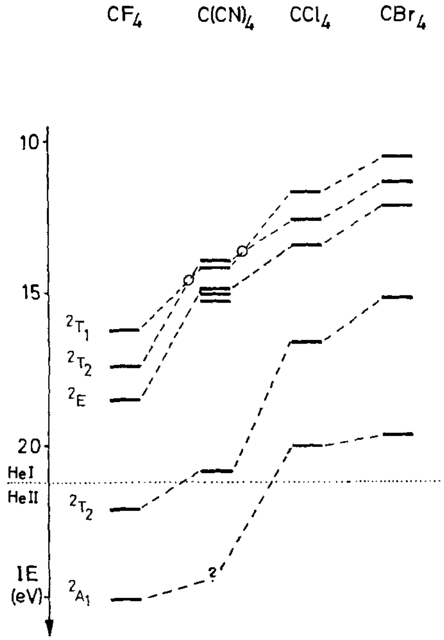

Fig. 3. *Comparison of orbital energies for CX_4-species* (X=F, CN, Cl, Br)

The postulated inversion of the $^2T_1/^2T_2$ radical cation states (Fig. 3) is straightforwardly explained by the additional 8 valence electrons of $C(CN)_4$, giving rise to two more bands in the low energy region, and the resulting $^2T_2/^2T_2$ repulsion.

Attempts to reproduce the experimentally deduced orbital sequence by quantum-chemical calculations met with difficulties. Neither standard *ab-initio* calculations at the STO-3G or 4-31G level nor semi-empirical calculations using the MINDO/2-, MINDO/3- or CNDO-procedures led to convergence. Excessive trials using various different initial guesses for the P-matrices led finally to convergence of MINDO/2, however with unsatisfactory results not to be discussed. Obviously, even though $C(CN)_4$ is non-polar by symmetry, the non-uniform charge distribution among the atoms requires a judicious choice of the SCF-starting point. Only the PE.-spectroscopically parametrized modified CNDO-version [14] converged, but as usual the results place the $n_N(\sigma)$-orbital in between the π_{CN}-orbitals:

MO	$\pi_{CN}(4t_2)$	$\pi_{CN}(1t_1)$	$n_N(3a_1)$	$n_N(3t_2)$	$\pi_{CN}(1e)$	$\sigma_{CC}(2t_2)$	
$\varepsilon_J^{CNDO^{mod.}}$ (eV)	−12.86	−13.66	−14.91	−15.09	−15.37	−23.43	(5)

The ionisation from the $\sigma_{CC}(2t_2)$-orbital is predicted to occur at 23.43 eV, in good agreement with the broad band peaking at 21.02 eV in the He(II)-spectrum of $C(CN)_4$. The low energy band shapes exhibit a rather close resemblance to those observed in the He(I)-record (Fig. 2).

The calculated CNDO (mod.) atomic charges,

$$\overset{+0.13}{C} - \overset{+0.22}{C} \equiv \overset{-0.26}{N} \qquad (6)$$

especially the considerable positive ones at the cyano carbon atoms, are in accord with the somewhat puzzling reactivity of tetracyanomethane as exemplified by the reaction with LiCl (1), and in more general terms, as if it 'contains a positive cyano group' [2].

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REFERENCES

[1] *H. Bock & W. Fuss*, Chem. Ber., *109*, 799 (1976).
[2] *E. Mayer*, Mh. Chem. *100*, 462 (1969) and *101*, 846 (1970).
[3] *H. Obernhammer*, Z. Naturforsch. *A 26*, 2043 (1971).
[4] *K. Rubin & R. Rudman*, J. chem. Physics *76*, 3973 (1972).
[5] *P. Rosmus, H. Stafast & H. Bock*, Chem. Physics Letters *34*, 275 (1975).
[6] *H. Stafast & H. Bock*, Tetrahedron, in print.
[7] *H. Stafast & H. Bock*, Z. Naturforsch. *B28*, 746 (1973).
[8] *D. C. Frost, F. G. Herring, C. A. McDowell & F. A. Stenhouse*, Chem. Physics Letters *4*, 533 (1970).
[9] *C. R. Brundle, M. B. Robin & H. Basch*, J. chem. Physics *53*, 2196 (1970).
[10] *A. W. Potts, H. J. Lempka, D. G. Streets & W. C. Price*, Phil. Trans. Royal Soc. London *A 268*, 59 (1970).
[11] *R. N. Dixon, J. N. Murrell & B. Narayan*, Mol. Physics *20*, 611 (1971).
[12] *H. Stafast*, Thesis, University of Frankfurt 1974.
[13] *R. Manne*, Chem. Physics Letters *5*, 127 (1970).
[14] *J. Kroner, D. Proch, W. Fuss & H. Bock*, Tetrahedron *28*, 1585 (1972).
[15] *H. Stafast & H. Bock*, Chem. Ber. *107*, 1882 (1974).