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The outer valence ionization energies of thiazyl cyanide

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Abstract. – We present a theoretical *ab initio* investigation of the low-energy valence Photo Electron (PE) spectrum of NSCN, a novel thiazyl compound recently synthetized, by using many-body post-SCF electronic structure methods. To account for correlation and relaxation effects neglected within the Koopmanns' theorem approximation, we used the SAC/SAC-C.I. theory in calculating the lowest ionization energies. Correlation effects are quite important to reliably understand the recorded PE intensity of NSCN. We are able to propose a different assignment of the entire outer valence PE spectrum of NSCN which seems more consistent and in better agreement with the experiment. We also discuss similarities and differences in the ionization energies of NSCN and closely related molecules (cyanogen and thiazyl halides).

Introduction. – Thiazyl cyanide is a novel, short-lived, gaseous compound synthetized a few years ago via eterogeneous (solid-gas) exchange reaction of AgCN and gaseous NSCl [1],[2]. To its identification, aside from I.R. and microwave measurements [1], HeI PE spectrum proved instrumentally important [2]. Out of 10 distinct experimental sharp peaks, three of them were imputed to NSCl's I.Es. (10.96, 11.80 and 14.5 eV) and the recorded intensity at higher energy ($\geq$ 15 eV) was ascribed to ionizations of contamination compounds and/or of spectrometer calibration gases (Ar and N_2). However, the *ab initio* SCF-based assignment (8a′, 2a″, 7a′ and 1a″, 11–15 eV binding energy) proposed in ref. [2] for the first four ionization energies (I.Es.) is probably of little help to even qualitatively understand the recorded bands of the spectrum which extends up about 18 eV. Indeed, it is unsafe and unappropriate to dismiss recorded peaks and structures as due to impurities' bands basically relying on highly qualitative SCF data, and to make assignments by direct use of the Koopmanns' theorem (KT) approximation. This description of the lowest-energy part of the PE spectrum of NSCN departs from the more usual view [3], [4] (7a′, 6a′, 2a″ and 5a′) in the thiazyl halides series (NSX, X = F, Cl, Br, I) to which NSCN might be related. In addition, this assignment left undetermined the apparent shoulder, at 13.21 eV, of the most intense band peaked at 13.52 eV. Chemically,

NSCN is not only close to NSF or NSCl but also to cyanogen, N_2C_2, whose outer valence PE spectrum has since long been measured and understood in detail [5], [6]. It was then found by Cederbaum *et al.* [6] that in the $(CN)_2$ PE spectrum many-body effects are large and essential to correctly understand the experiment. This is also the case for NSF [4], though to minor extent. Many-body effects have long been shown [7] to be really important not only in the inner valence region, but also for low-lying molecular ionizations. Therefore we fairly expect that many-body effects would also play a major role in the valence PE spectrum of thiazyl cyanide which, on the other hand, can be well considered as a *perturbed* cyanogen. In the following we shall further exploit this concept, and we shall argue that basically the outer valence PE spectrum of NSCN can be understood qualitatively well in terms of that of cyanogen, and with the help of reliable theoretical results we shall better understand its PE spectrum. To this end we used the symmetry-adapted cluster (SAC) and SAC-C.I. [8]-[10] many-body theory.

Computational details. – *Ab initio* all-electron fixed-geometry SCF calculations of NSCN were performed at simple and polarized double- to triple-ζ quality basis sets level with the HONDO8 program package [11]. Being its experimental geometry unknown yet, we adopted the geometrical parameters for a planar, quasi–two-sides, configuration as obtained in ref. [2] via an SCF 6–31 G* polarized basis set energy optimization ($d_{\mathrm{NS}} = 149$ pm, $d_{\mathrm{SC}} = 179$ pm, $d_{\mathrm{CN}} = 114$ pm, $\theta(\mathrm{NSX}) = 109.3°$, $\theta(\mathrm{SCN}) = 176.9°$, ϕ(dihedral)(N-S, C-N)$= 180°$). For the here reported many-body results basis sets were as follows. The triple-ζ quality Cartesian Gaussian basis sets were taken from HONDO8 ($11s6p/5s3p$(C, N) and $13s10p/6s5p$ (S)) to which a set of polarization d-functions ($\alpha_d = 0.072$(C), 0.98(N), 0.6(S)) was added in. The calculated total energy (in a.u) was: -544.20782. SAC and SAC-C.I. calculations for ground and ionized states of NSCN were carried out within the SAC(85) implementation [12], for which only ionic states which are dominantly one-hole configurations can correctly be treated.

Results and discussion. – NSCN molecule may be considered on chemical grounds a pseudo-thiazyl halide. Since the SC and CN bonds are practically aligned with one another, it should have the same geometry as the one of NSF and heavier thiazyl halides (C_s symmetry, A′ irreducible representation ground state). The electron energy levels structure and bonding properties are easily discussed considering its 20 valence electrons which are allocated into eight MOs of a′ symmetry and two MOs of a″ symmetry. The LUMO, of a″ symmetry too, is largely localized on the NS moiety, and has a thin energy (less than 0.2 eV). The SCF ordering sequence, in decreasing energy, of the valence MOs is: $\ldots 3a'4a'5a'1a''6a'7a'2a''8a'$. When using unpolarized basis sets, this sequence is pretty independent of basis sets. The two strongly bonding a″ symmetry MOs have out-of-plane π-character and, at variance of the corresponding MOs of NSF, are delocalized on the NS and CN moieties with major components on sulfur. Quite understandbly they appear sensitive to polarization functions and, within basis sets inclusive of the latter, an ordering inversion of the 6a′ and 1a″ MOs energies occurs. On the contrary a′ symmetry MOs energies are substantially unaltered by polarization functions, while showing considerably many-body effects. As pseudo-thiazyl halide, NSCN exhibits a valence PE spectrum which is blue-shifted with respect to that of NSCl, and whose lowest I.Es. lie between those of NSF and NSCl. Because the CN substituend, regarding its electron withdrawing power, is closer to fluorine than to chlorine, one may argue that, at least in its first few I.Es., NSCN should resemble NSF [3]. This view, in some sense, is backed by the weak antibonding or no-bonding character of the first outermost MOs of the two molecules, which are essentially localized in the NS moiety. On the other hand, as was mentioned above, the NSCN molecule may be considered a perturbed cyanogen. Besides a different geometry, NSCN, in the valence region, has only one more occupied MO than N_2C_2. This is the 8a′

MO (*i.e.* the HOMO), mainly dominated by sulfur $3p$ and $3s$ atomic orbital, which is specific of NSCN and of the other thiazyl halides as well. Disregarding this MO, if the perturbation which changes cyanogen into NSCN is relatively small, we may qualitatively correlate the nine valence MOs of both molecules through a one-to-one correspondence. For our purposes though, in both molecules we consider only the six SCF MOs whose energies lie below 18–19 eV. We expect the SCF energy sequence of cyanogen, $1\pi_g$(13.60 eV), $1\pi_u$(16.42 eV), $5\sigma_g$(16.93 eV) and $4\sigma_u$(17.35 eV)[6] to give rise in NSCN to the SCF MOs energy sequence, 2a″, 7a′, 1a″, 6a′, 5a′, 4a′. Thus we may foresee that the 2a″ and 7a′ MOs energies should lie around 13.5 eV, those of the 1a″ and 6a′ MOs around 16 eV and so on. All this, of course, is very qualitative, but it certainly goes in the right direction. Indeed, the SCF MOs energies of NSCN reproduce this pattern quite well. N_2C_2 molecule has a low-energy PE spectrum showing four bands up to about 16 eV which KT approximation erroneously assigns, in increasing energy, to $1\pi_g$, $1\pi_u$, $5\sigma_g$, $4\sigma_u$ MOs ionizations. Refined *ab initio* GF-based calculations [6] instead yield the correct MOs energy sequence ($1\pi_g$, $5\sigma_g$, $4\sigma_u$, $1\pi_u$) and, within a few tenths of eV, match the experimental energies. In this case, very strong many-body effects pull down the energy of the $5\sigma_g$ and $4\sigma_u$ MOs much more than that of the $1\pi_u$ MO, whereas the HOMO ($1\pi_g$) energy is comparatively very little moved from its SCF value. If, as it seems here, perturbations leading to NSCN from N_2C_2 are small with respect to the many-body effects, the SCF MOs energy sequence of NSCN is altogether wrong. Furthermore, we should expect many-body effects to qualitatively act on the NSCN's PE spectrum in the same way and roughly in the same amount as we have seen in that one of cyanogen. Along this way, we also might tentatively predict the outcome of many-body calculations on NSCN's I.Es.

In NSCN, the π-character 2a″ component of the quadratic degenerate $1\pi_g$ MO of cyanogen will be very little moved in energy by many-body effects. The 7a′ component, instead exhibiting a mixed in plane π-σ character, shall probably show a somewhat greater sensitivity to correlation than its mate and its energy shall change by a few tenths of eV from its SCF value. It is difficult, however, to say whether these energy shifts (2–4 tenths of eV) on the pair of 2a″, 7a′ MOs shall tend to close or to widen the half eV energy separation calculated at SCF level. Rough arguments would suggest the first possibility.

Let us consider now the $1\pi_u$ MO. This will tranform, in NSCN, into the pair of the 1a″ and 6a′ MOs. As in the previous case 1a″ MO shall experience very little many-body energy shift, while this is not the case for its mate, the 6a′ MO. This orbital shall take the most of the many-body energy red-shift ($\simeq$ 1 eV) suffered by his parent MO ($1\pi_u$) in the cyanogen, thus leading it to precede its mate (the 1a″ MO). The red-shift of about 2.5 eV, affecting the SCF energies of the $5\sigma_g$ and $4\sigma_u$ MOs, is the most dramatic many-body effect seen in the cyanogen's PE spectrum. To these MOs correspond, in NSCN, the 5a′ and 4a′ MOs, respectively. Should this large energy shift also realize in the NSCN PE spectrum, we will obtain the following MOs energy ordering: 8a′, 2a″, 7a′, 5a′, 6a′, 1a″, 4a′. Moreover, were we confident on the qualitative and/or semi-quantitative correctness of these rationales, we could even try to use this MOs energy ordering for assignment purposes of the NSCN PE experimental spectrum.

In fig. 1 we report some results of our SCF and SAC-C.I. calculations on NSCN vertical valence I.Es. Neglecting the sharp shoulder at 13.21 eV, KT assignment, regardless of the basis set, leads for the first four bands at 11.33, 13.52, 14.02 and 14.97 eV to the following ordering (in increasing energy): 8a′, 2a″, 7a′ and 1a″. This assignment follows the analogous, but wrong, pattern of the *ab initio* SCF calculated NSF MOs energies [3], [4]. Here the calculated energy separation between 2a″(13.25 eV) and 7a′(13.79 eV) MO's energies indeed matches that one between the second (13.52 eV) and the third (14.02 eV) experimental peak, and this was also found in the NSF PE spectrum [3]. But in this way the strong shoulder at 13.21 eV remains unassigned. This shoulder, on the other hand, cannot be ascribed to NSCl, as

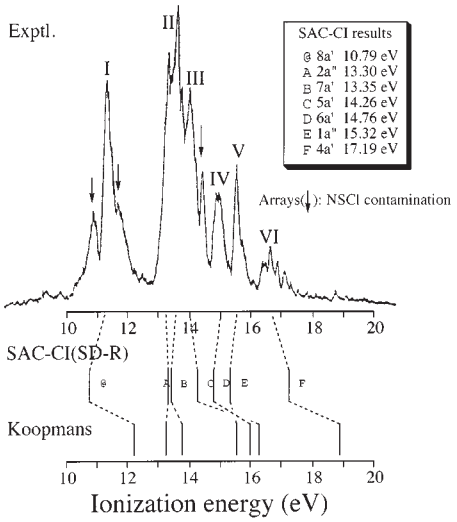

Fig. 1. – Experimental (ref. [2]) and calculated PE spectra of NSCN.

instead is the case for other peaks. At higher ionization energy, KT ionic states 6a′(16.0 eV), 5a′(16.3 eV) and 4a′(18.92 eV) in no way can be related to the spectral features of spectrum in this energy region.

Polarized double- and triple-ζ SAC-C.I. results indicate three main ionic states with energy smaller than 14 eV. Among these, it is the HOMO energy which undergoes to relatively strong many-body effects ($\simeq$ 1.2 eV), whereas 2a″ and 7a′ MOs energies are little affected (0.2–0.3 eV). This disuniformity is quite common in calculating theoretical *ab initio* many-body molecular I.Es., particularly when the LUMO is of π symmetry and has very small energy as is the case here. How this comes about in molecular ionizations has been nicely shown, within the GF-based many-body theory, in ref. [13]. It involves the symmetries and localization properties of the relevant MOs together with the transition densities and MOs energy differences. On the other hand, as was discussed above, 2a″ and 7a′ ionizations suffer scarce many-body energy shifts for they originate from the $1\pi_g$ MO of cyanogen. Upon inclusion of relaxation and correlation effects, the half eV energy gap between their SCF energies tends to vanish leading thus to a quasi-degeneracy. This gap-closing effect on the two calculated ionic states energies is found constantly within different SAC-C.I. calculations and, apparently, is a combined effect of polarization functions and electron correlation.

Looking at the PE experimental spectrum below 14 eV, we first find a slightly asymmetric band peaked at 11.33 eV with two accompanying minor peaks at little smaller and greater energy (see fig. 1). On the whole, this band hardly shows any vibrational progression which is absent or unresolved in the experiment. On the other hand, these minor peaks are, very probably, the first two ionizations (7a′ and 6a′) of unreacted NSCl. It is then direct to assign this band to the 8a′ ionization of NSCN. For it our SAC-C.I. calculations has given an energy around 10.8(9) eV. To compare this vertically calculated value to the band's maximum (11.33 eV) may not, in general, be safe and appropriate [7]. On the other hand, aside from the NSCl peaks, the band looks quite symmetric, and one could then assume the band's maximum to be the vertical value of the first ionic state of NSCN. If so, the discrepancy between theory and experiment, at worse, is 0.5 eV. Part of it could certainly be decreased by basis set enlargments especially on sulfur which dominates the 8a′ MO. Next we have a

broad very intense bands' envelope extending from about 13 to 14.7 eV. This bands' system, which certainly contains several ionic states, shows no significant vibrational structure too. Very probably at least another ionization of NSCl (the one at 14.6 eV and perhaps that one at 13.8 eV) is contained on it. Within this energy domain our many-body calculations have yielded three main ionic states. Namely the 2a″, 7a′ and 5a′ MOs ionizations at energy 13.30, 13.35 and 14.26 eV, respectively. The 2a″ and 7a′ ionizations appear quasi-degenerated, which is not unexpected according to the discussion carried out above. Quite surprising from a SCF viewpoint, the next ionic state is the 5a′ MO ionization which suffers, analogously to the $5\sigma_g$ MO energy of cyanogen, a very large red-shift of about 2.2 eV. We realize here the soundness of our physically comparative analysis of the NSCN PE spectrum by arguing on that one of his *parent* compound, *i.e.* cyanogen. Therefore, we assign, on quite firm grounds, this bands' system the ionic states 2a″, 7a′ and 5a′. Being the first two ionizations practically calculated degenerate, we are unable, within the uncertainty of our results, to assign the shoulder at 13.21 eV to the first one (2a″) or the second one (7a′) of this pair of ionic states. In this respect, NSCN outer valence spectrum looks like those of heavier thiazyl halides in which the corresponding ionizations (2a″ and 6a′), though different in nature, appear in the calculations [14] degenerate too and in the experiments [2], [15] unresolved. From 15 eV up to 18 eV the recorded intensity of the NSCN PE spectrum shows three bands of medium or relatively weak intensity. The first one, symmetric and relatively broad (0.5 eV) is centered at 14.97 eV and does not show vibrational structure. By experimentalists [2] it was assigned to the 1a″ ionization via direct KT application. According to our SAC-C.I. calculations, instead it has to be assigned to 6a′ ionization for which we have calculated an energy of about 14.8 eV. This ionization, under many-body effects, behaves somewaht similarly to 5a′ ionization and parallels the $4\sigma_u$ of cyanogen. At 15.50 eV we find a sharp slightly asymmetric band and between 16 and 18 eV a broad low-intensity quite structured band exhibiting vibrational progression and/or probably secondary (shake-up) ionization events. Because in this energy range KT usage is meaningless, only many-body calculations might be of help to understand the experiment. In ref. [2] this part of the spectrum was unassigned and simply dismissed as due to contamination. According the present study, instead we would assign the band at 15.5 eV to 1a″ ionization and the one around 17 eV to 4a′ ionization of NSCN which we have calculated at 15.32 and 17.19 eV, respectively. We see, therefore, that the many-body calculations here presented have led to the following global assignment of the outer valence PE spectrum of NSCN: 8a′, 2a″, 7a′, 5a′, 6a′, 1a″, 4a′. This assignment is exactly the same as the one proposed above and obtained by qualitative rationales based on the cyanogen experimental and GF-based theoretical PE spectra [5], [6]. Agreement with the experiment, in so far as the vertical ionizations energies could have been unambiguously identified, seems on the whole satisfactory.

A major point of great relevance in understanding the PE experimental spectra is certainly the presence of non-Koopmanns ionizations. This issue was not explicitly raised in the present study. There are good reasons justifying this attitude. Many-body calculations on cyanogen within the 2ph-TDA theory of Cederbaum *et al.* [16], and particularly aimed at searching satellite lines in its spectrum, have indicated the absence of such secondary ionizations up to about 18 eV and the substantial validity of one-particle model to ionization for the first four ionic states. These conclusions, at least in great part, should also be substantially valid for the ionic states of NSCN up to, let us say, 16–17 eV. Around 17–18 eV things might be different. Preliminary *extended* SAC-C.I. calculations [17], indeed, would indicate the presence of several satellite lines with appreciable relative intensity already populating the PE spectrum of NSCN from 16 eV upwards. This diversity, between NSCN and N_2C_2, in some minor and subtle aspects of their PE spectra, after all is hardly unexpected. The different geometry, the

greater density of excitable 2h1p configurations at relatively lower energy than in cyanogen should have a certain bearing in some features of the recorded intensity. More refined and different experiments (HeII PE spectra, for example), however, should be carried out, and with the help of very accurate many-body calculations the satellite lines structure of NSCN could hopefully be understood.

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