Valence Ionization Spectra of Disubstituted *s*-Tetrazines: Strong Correlation Effects Induced by Substitution

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Abstract: We have calculated the low-energy valence ionization energies of *s*-tetrazine and four of its disubstituted compounds within two different approximations to the one-particle Green's function, namely the OVGF (Outer Valence Green Function) and the ADC(3) (full third-order approximation to the so-called Algebraic Diagrammatic Construction scheme) methods. The following substituents have been considered, OH, OCH_3, SH, and NH_2. In the present paper the trend of the ionization energies along the series of these molecules is studied and correlated with the electron-donor character of the substituents. Interesting phenomena can be observed in these molecules, e.g. the relative ordering of n and π ionizations, strong reduction of the relative intensity of the bands for most ionization processes, and more important, the appearance of satellite lines at much lower binding energy than was found for the parent molecule *s*-tetrazine. Our calculations confirm that in strong electron-donor disubstituted *s*-tetrazines the first line of the PES is of π symmetry in accord with Gleiter et al.[3] The agreement with available experiments (*s*-tetrazine and dimethoxy-*s*-tetrazine) is in general qualitatively good and for the lowest ionization energies excellent. For the other molecular systems investigated we are not aware of experimental data on ionization energies. Nonetheless the close similarity between these molecules and some of those studied by Gleiter et al. helps in understanding and clarifying some problems that are encountered in the analysis of the PE spectra of the latter ones. The results of our calculations suggest that the n_2 ionization, for which there are problems of identification in the experimental spectrum in some disubstituted *s*-tetrazines, is subject to a breakdown of the molecular orbital model. This leads to low-lying satellite lines to which a clarifying discussion in simple terms is devoted.

I. Introduction

It is one of the aims of Quantum Chemistry to illustrate and to clarify the nature and validity of empirical concepts that find application in the world of experimental chemistry. Among these the concept of electron-donor/acceptor group is one of the most useful ones to rationalize the chemical behavior of functional groups with respect to chemical reactions. Important in this context is also the change in molecular properties when a group of atoms is substituted by another. For a deeper understanding of this concept, a knowledge of the electronic structure of the molecular systems is required. Within the usual Born-Oppenheimer Hamiltonian, the concept of electron-donor/acceptor group may usefully be analyzed in terms of the valence MO's, their charge distribution, and localization properties on the functional groups. This knowledge can be acquired by PES[1] techniques and/or by semiempirical or ab initio quantum-mechanical molecular electronic structure calculations (see e.g. ref 2). Gleiter et al.[3] have recently undertaken a study by photoelectron (PE) spectroscopy with He I radiation on a series of disubstituted *s*-tetrazines to investigate the ordering of the ionization energies as well as the energy shifts on the ionization energies with respect to the parent molecule brought about by electron-donor/acceptor substituents. This experimental study was also supplemented with HAM/3[2c] calculations of the outer valence ionization energies. According to this work the HOMO of the disubstituted *s*-tetrazines with strong electron-donor groups, like alkylamino groups, has π character, whereas in the *s*-tetrazines disubstituted with alkyl or electron-acceptor groups it is of type n. A strong electron-donating group seems to lead to an inversion of the ordering of the first two ionization energies with respect to the ordering of the *s*-tetrazines substituted with electron-withdrawing groups, but it is not clear what happens to the next two bands. In particular it is seen from the He I PES of ref 3 that for dimethylamino- and methylmercapto-*s*-tetrazines it is difficult to identify a fourth band below 11 eV in the PE spectra.

The ab initio Green's Function (GF) investigation presented here aims at understanding the structure of the ionization spectra, the orbital origin of the low-energy valence ionization energies of the molecules studied here, i.e. *s*-tetrazine (I), dihydroxy-*s*-tetrazine (II), dimethoxy-*s*-tetrazine (III), dimercapto-*s*-tetrazine (IV), and diamino-*s*-tetrazine (V) (see Figure 1). For relatively large molecules the interpretation of the PE spectra runs easily into difficulties, because of limited experimental resolution and because of the many bands that lie very close to one another. Theoretical calculations, either semiempirical or ab initio, can often be of help to resolve some of these problems, but the uncertainties caused by the parameters in the semiempirical methods and the restricted basis sets which have to be used in the ab initio methods may limit the accuracy of the predictions. The GF method has proved, however, in spite of these problems a very reliable tool for the interpretation of the PE spectra of even large molecules.[4]

The ionization energies of compounds I-V in the low-energy valence region are presented in this article. Two GF approaches are employed here, namely the outer valence GF (OVGF) and the ADC(3) (Algebraic Diagrammatic Construction) methods.[5,6] The latter one has been previously referred to as the extended two-particle-hole Tamm Dancoff Approximation (extended

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(1) Turner, D. W.; Baker, C.; Baker, A. D.; Brundle, C. R. *Molecular Photoelectron Spectroscopy*; Wiley Interscience: New York, 1970. Rabalais, J. W. *Principles of Ultraviolet PE Spectroscopy*; Wiley Interscience: New York, 1977.

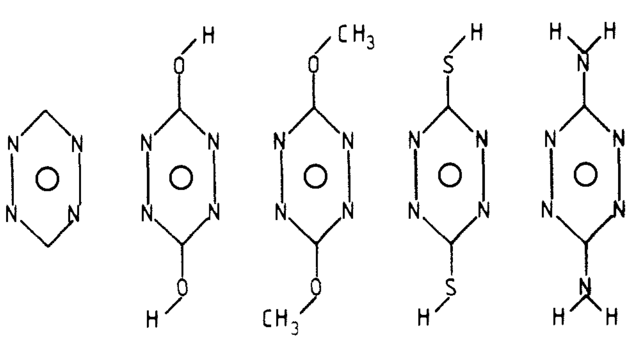
(2) (a) Cederbaum, L. S.; Domcke, W. *Advances in Chemical Physics*; Prigogine, I., Rice, S. A., Eds.; Wiley Interscience: New York, 1977, Vol. 30. (b) Niessen, W.; Schirmer, J.; Cederbaum, L. S. *Computer Phys. Rep.* **1984**, *1*, 39. (c) Lindholm, E.; Asbrink, L. *Lecture Notes in Chemistry: Molecular Orbitals and their Energies studied by HAM/3*; Springer: Heidelberg, 1980. (d) Bigelow, R. *Chem. Phys.* **1980**, *80*, 45.

(3) Gleiter, R.; Schelman, V.; Spanget-Larsen, J.; Fischer, H.; Neugebauer, F. *J. Org. Chem.* **1988**, *53*, 5757.

(4) von Niessen, W.; Cederbaum, L. S.; Schirmer, J. *J. Electron Spectrosc.* **1986**, *41*, 235.

(5) Cederbaum, L. S. *Theor. Chim. Acta* **1973**, 31, 329; *J. Phys. B* **1975**, *8*, 290.

(6) Schirmer, J.; Cederbaum, L. S.; Walter, O. *Phys. Rev. A* **1983**, *28*, 1237.



I II III IV V

Figure 1. Molecular systems investigated in the present article.

2ph-TDA).[7] These GF techniques to calculate the ionization energies of molecular systems have been presented and discussed in detail elsewhere.[2a,b,6] We only recall here that both methods, for main ionic states, are exact up to third order of perturbation theory in the residual electron–electron interaction and contain additional contributions of higher order. The ADC(3) method has been shown to be an appropriate theoretical framework to investigate ionic states even when a one-particle model of ionization does not apply and ionic satellite states may acquire substantial spectral intensity. For compounds II–V no ab initio calculations have been reported in the literature. For *s*-tetrazine (I) a 2ph-TDA(ADC(2)) calculation has been reported in ref 15. In section II we give some computational details, and in section III we present and discuss the calculated low-energy PE spectra of compounds I–V. A discussion on the appearance of low-lying satellite peaks in some of the PE spectra is presented in section IV. A summary and concluding remarks are given in section V.

II. Computational Details

The ab initio SCF calculations of the molecules were performed with the program system MUNICH.[8] The geometries were optimized with the AMPAC/MNDO[9] method. For *s*-tetrazine, the experimental geometry of ref 10 was used instead. We adopted the AMPAC/MNDO geometries because we are not aware of experimental data on II and IV and because we thought it relevant to the investigation to do the calculations with geometries derived from a unique and consistent source. Experimental geometries of III and V have been published recently by Krieger et al.[11] Discrepancies between the experimental geometrical parameters and the corresponding ones obtained through the MNDO procedure are within 0.05 Å for bond distances and a few degrees for the planar angles. No noticeable changes in the ring's geometrical parameter are observed on going from *s*-tetrazine to the disubstituted compounds for the experimental data as well as for those optimized.

The basis sets (double-ζ) of Cartesian Gaussian functions were (9s5p)/(4s2p) for (C, N, O), (12s9p)/(6s4p) for S, and (4s)/(2s) for H. Exponential parameters and contraction coefficients were those of Huzinaga,[12] except for S where the data were taken from Veillard.[13] This expansion resulted in 64, 84, 112, 100, and 88 MO's for compounds I–V, respectively. For *s*-tetrazine we also augmented this basis set with a d-type function on C and N ($\alpha = 0.6$ and 0.7, respectively) and a p-type function on H ($\alpha = 0.75$), obtaining thus 106 basis functions. Core occupied MO's and their unoccupied counterparts were neglected in all GF calculations. The total SCF energies and the energies of the lowest occupied valence MO's of I–V are reported in Tables I–IV together with the GF results. In these tables the π and n ionic states are numbered in increasing energy according to their SCF values. For I the SCF and OVGF results performed with the double-ζ basis set listed in Table I were taken from ref 15, while the ADC(3) results update the 2ph-TDA-(ADC(2)) description of the ionic states reported in this latter reference.

For *s*-tetrazine within the two used basis sets we took into account all of the occupied (15) valence orbitals in carrying out the GF calculations. For the smaller basis set we performed the ADC(3) calculation including 35 virtuals MO's as it was done in ref 15 for the corresponding OVGF calculation with the same basis set. Neglecting core-occupied MO's and their virtual counterpart, the basis set was practically exhausted in the calculations with both GF methods. Only the four highest in energy valence virtual orbitals were indeed neglected. By using the larger (polarized) basis set we were compelled to neglect a greater number of valence virtual MO's to make reasonably limited the needed CPU store and time. Therewith we took 57 out of 81 virtual valence MO's in the OVGF calculation, but we left unchanged the number (35) of virtual MO's included in the ADC(3) calculation. This was done to put in clear evidence the effect of the polarization functions on the calculated ionization energies and corresponding relative intensities. However, a greater number (51) of virtual MO's was taken into account by carrying out an ADC(3) calculation within the so-called Davidson Diagonalization Approach (DDA)[14] to solve for the one-particle GF. Indeed the sofar referred ADC(3) calculations were performed within the so-called Pole Search Algorithm (PSA) method.[2b] Both methods to solve for the poles of the GF matrix are exact methods and yeld identical results when the same basis set is used. Discrepancies in the results of the two procedures are only due to the different number of orbitals used in the actual calculation or other built-in computational simplifications such as configuration selection. The PSA procedure has the advantage that all eigenvalues lying in any given energy interval can be computed, but it becomes inefficient if most of the matrices are not diagonally dominant. For *s*-tetrazine we, therefore, restricted ourselves to lesser virtual orbitals when using the PSA procedure. More orbitals can be included within a reasonable numerical effort when using the DDA technique and, therefore, more accurate results can be achieved with respect to the PSA ones. In fact within the DDA all of the 2h1p and 2p1h configurations stemming from the used MO space are taken into account when constructing the self-energy matrices of the Green's function matrix. For the MO space used the dimensions of the matrices, which were diagonalized by using the DDA technique for each irreducible representation of the D_{2h} point group symmetry, ranged between six and seven thousand. But only the lowest ten eigenvalues thereof were calculated. Unfortunately this procedure has the disadvantage that it usually is restricted to the lowest eigenvalues and that there is no guarantee that all eigenvalues in a given energy range can be found.

In the calculations with both GF methods, for the ionization energies of II–V molecules we took into account, as for I, all of the occupied valence MO's, that is 21 (for II, IV, V) and 27 (for III) MO's. In the OVGF (ADC(3)) calculations we included 39 (22), 23 (20), 39 (22), and 43 (28) virtual MO's for the molecules II–V, respectively. As the OVGF method does not require the construction or the diagonalization of large matrices it turns out it is possible to take more or even all virtual MO's into account. It is seen indeed that, with the exception of compound III, the greater part of the virtual MO's space was included. In view of the qualitative results which in general arise by using a double-ζ basis set without polarization or diffuse functions and in view of the fact that we are studying the low-energy region of the PE spectra, we considered it less important to exhaust completely the orbital space.

Within the ADC(3) method, because it requires the construction and diagonalization of matrices, whose dimensions increase enormously with the number of occupied and virtual MO's, a more severe cutoff than the one used in the OVGF method was needed. We used the PSA procedure throughout the calculation for compounds II–V. These technical simplifications may have, of course, some consequences on the accuracy of the calculated quantities (i.e. energy and corresponding relative intensity of the ionic states). This loss of accuracy can be checked in part by comparison of the ADC(3) results for the main lines to the corresponding OVGF values. By this check we were thus aware that the energy cutoff used in the ADC(3) calculations for II, III, and IV had negligible influence on the obtained results for the main lines. However, this was not the case for V. We overcame the difficulties by resorting to the DDA procedure where we could take the same number of orbitals into account as in the OVGF calculation. The expected agreement for the main lines between the two GF methods was thus restored.

On the other hand since we are dealing with the low-energy region of the PE spectra, it can be reasonably argued that the loss of accuracy due to these computational simplifications should remain somewhat limited.

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(7) Schirmer, J.; Cederbaum, L. S. *J. Phys. B* **1978**, *11*, 1889.

(8) Diercksen, G. F.; Kramer, W. P. MUNICH Molecular Program System, Special Technical Report; Max Planck-Institut fuer Physik und Astrophysik. Diercksen, G. H. F. *Theor. Chim. Acta* **1974**, *33*, 1.

(9) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899. Dewar, M. J. S.; Zoebisch, E. G.; Heady, E. F.; Stewart, J. J. J. *J. Am. Chem. Soc.* **1985**, *107*, 3902.

(10) Merer, A. J.; Innes, K. K. *Proc. R. Soc. A* **1967**, *302*, 271.

(11) Krieger, C.; Fischer, H.; Neugebauer, F. *Acta Crystallogr.* **1987**, *C43*, 1320, 1412.

(12) Huzinaga, S. *J. Chem. Phys.* **1965**, *42*, 1293.

(13) Veillard, G. *Theor. Chim. Acta* **1968**, *12*, 405.

(14) Davidson, E. R. *J. Comput. Phys.* **1975**, *17*, 87. Liu, B. NRCC Report LBL 8158, 1978. Actually we used a block-Davidson routine that was coded by F. Tarantelli.

(15) von Niessen, W.; Kraemer, W. P.; Diercksen, G. H. F. *Chem. Phys.* **1979**, *41*, 113; *J. Chem. Phys.* **1977**, *66*, 4893.

Table I. Ionization Energies (eV) and Corresponding Relative Intensities of *s*-Tetrazine[a] in the Low-Energy Valence Region

orbital[b]	$-\epsilon_i$	OVGF	ADC(3)[e]	ADC(3)[f]	exptl	
$n_1\ 2b_{3g}(6a_g)$	11.36	9.42 (0.90)	9.80 (0.89)	9.54 (0.89)	9.7[c]	9.7[d]
$\pi_1\ 1b_{2g}(2b_g)$	11.98	12.05 (0.90)	12.32 (0.88)	12.01 (0.89)	11.9	12.1
$n_2\ 3b_{1u}(6b_u)$	14.47	12.11 (0.87)	12.44 (0.81)	12.20 (0.81)	12.1	12.1
$n_3\ 4a_g(5a_g)$	14.52	12.82 (0.90)	13.15 (0.88)	12.86 (0.87)	12.8	12.8
$n_4\ 3b_{2u}(5b_u)$	15.36	12.97 (0.87)	13.20 (0.77)	12.95 (0.78)	13.3	13.4
$\pi_2\ 1b_{1g}(1b_g)$	13.50	13.23 (0.88)	13.59 (0.85)	13.19 (0.86)		13.5
$3b_{1u}(6b_u)$			14.33 (0.04)	14.13 (0.04)		
$3b_{2u}(5b_u)$			14.82 (0.06)	14.60 (0.07)		
$\pi_3\ 1b_{3u}(1a_u)$	17.61		16.16 (0.59)	15.95 (0.61)	15.8	15.8
$3b_{1u}(6b_u)$			16.26 (0.02)	15.96 (0.01)		
$1b_{3u}(1a_u)$			16.28 (0.01)	16.07 (0.01)		
$3a_g(4a_g)$			16.78 (0.01)	16.63 (0.01)		
$3a_g(4a_g)$				16.94 (0.01)		
$1b_{3u}(1a_u)$			17.31 (0.08)	16.97 (0.10)		
$3b_{2u}(5b_u)$			17.77 (0.01)	17.45 (0.03)		
$2b_{1u}(4b_u)$			17.74 (0.07)	17.52 (0.09)		
$2b_{2u}(3b_u)$			18.00 (0.04)	17.63 (0.01)		
$2b_{1u}(4b_u)$	19.32		17.89 (0.77)	17.64 (0.75)		
$3a_g(4a_g)$	20.54		18.21 (0.65)	17.99 (0.60)		
$2b_{1u}(4b_u)$			18.55 (0.02)	18.37 (0.02)		

[a] Total SCF energy within the dz+p basis set: −294.5555 (au). [b] Symmetries in D_{2h} point group symmetry. The corresponding symmetries in C_{2h} are given in brackets. [c] Reference 16. [d] Reference 17. [e] A limited number of virtual orbitals and the PSA method have been used. [f] 51 virtual orbtials and the DDA procedure have been used (see text).

Table II. Effect of Polarization Functions on the Low-Energy Ionization Energies (eV) of *s*-Tetrazine within the OVGF and ADC(3) Methods[a]

	$-\epsilon_i$		OVGF		ADC(3)[e]	
orbital[b]	dz[c]	dz+p[d]	dz	dz+p	dz	dz+p
$n_1\ 2b_{3g}(6a_g)$	11.48	11.36	9.24 (0.90)	9.42 (0.90)	9.64 (0.88)	9.80 (0.89)
$\pi_1\ 1b_{2g}(2b_g)$	12.69	11.98	12.52 (0.91)	12.05 (0.90)	12.87 (0.87)	12.32 (0.88)
$n_2\ 3b_{1u}(6b_u)$	14.64	14.47	11.97 (0.87)	12.11 (0.87)	12.27 (0.81)	12.44 (0.81)
$n_3\ 4a_g(5a_g)$	14.57	14.52	12.64 (0.90)	12.82 (0.90)	12.93 (0.87)	13.15 (0.88)
$n_4\ 3b_{2u}(5b_u)$	15.67	15.36	12.89 (0.87)	12.97 (0.87)	13.04 (0.74)	13.20 (0.77)
$\pi_2\ 1b_{1g}(1b_g)$	13.95	13.50	13.47 (0.89)	13.23 (0.88)	13.92 (0.85)	13.59 (0.85)
$\pi_3\ 1b_{3u}(1a_u)$	18.23	17.61			16.75 (0.62)	16.16 (0.59)
$2b_{1u}(4b_u)$	19.77	19.32			18.23 (0.73)	17.89 (0.77)

[a] Main state energies only are reported. [b] Symmetries in D_{2h} point group symmetry. The correponding symmetries in C_{2h} are given in brackets. n and π states are numbered in increasing energy according to the SCF energies of basis set with polarization functions. [c] Double-ζ basis set (see section II for details). [d] Double-ζ basis set augmented with polarization functions. [e] A limited number of virtual orbitals and the PSA procedure have been used in these calculations (see section II for details).

In the next section, in discussing the GF results, we shall further comment on this aspect of our calculations.

Ionic states for molecules II–V were calculated up to about 22 eV binding energy, but we present and discuss our GF results for the ionic states below 16 (18 for *s*-tetrazine) eV.

III. Results and Discussion

a. *s*-Tetrazine. We revisit some problems that are encountered in the interpretation of the outer-valence PES of the parent system *s*-tetrazine. The interpretation of the outer-valence PES of *s*-tetrazine although essentially clarified contains some open questions. The first band in its spectrum originates from an ionization out of a n orbital.[15-20] Different interpretations have been suggested for the successive bands. In particular for the second band system it has remained unclear whether or not it contains the first π ionic main state. Gleiter et al. in ref 3, for example, conclude, on grounds of comparisons between the experimental PE spectra of I and those of the dimethyl- and diphenyl-*s*-tetrazines, that this band contains the π_1 and n_2 main ionic states, the latter one being a little bit higher in energy than the former, thus giving support to the early assignment of Almlöf et al.[18] On the other hand, the 2ph-TDA and the OVGF results discussed in ref 15 and computed with the unpolarized basis set give rise to different interpretations. According to the OVGF and also to the ADC(3) results (same basis set; see Table II) the π_1 ionic main state could well be hidden under the experimental peak at 12.8 eV, which should thus consist of π_1 and n_3 ionic main states. The n_2 derived ionic state is thus assigned to the band at 12.1 eV. The 2ph-TDA results can be instead better interpreted according to the idea that the π_1 and perhaps the n_2 main ionic states have to be found in the band around 12.1 eV. But we notice that the 2ph-TDA is less accurate than the OVGF and ADC(3) methods, and realizing the generally good description of the latter methods for the lowest five main ionic states, we would incline to assign π_1 to the band at 12.8 eV and n_2 to the band at about 12.0 eV, which thus should contain a main ionic state only. However, the discrepancies observed between the ADC(3) results and experiment for the two other π states may invalidate this rationale. It may also be that the energy of π_1 is overestimated. Because we almost exhausted the basis set in the OVGF and ADC(3) calculations, we can argue that the origin of the discrepancies with respect to the experiments must lie in the basis set used. The addition of polarization functions could probably reduce these discrepancies and clarify whether or not the π_1 state lies in the second band. This turned out indeed to be the case here.

The ADC(3) and OVGF calculations with the polarized basis set on I presented in this paper yield results that in principle and as is seen by a comparison with experiments (see Table I) are more accurate in several respects that the 2ph-TDA ones or the corresponding ADC(3) and OVGF results obtained without polarization functions (see Table II). Upon inclusion of the polarization functions one observes in fact that the n main ionic state energies

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(16) Fridh, C.; Asbrink, L.; Jonsson, B. O.; Lindholm, E. *Int. J. Mass. Spectrom. Ion Phys.* **1972**, *9*, 485.

(17) Gleiter, R.; Heilbronner, E.; Hornung, V. *Helv. Chim. Acta* **1970**, *55*, 255.

(18) Almlof, J.; Roos, B.; Wahlgren, U.; Johansen, H. *J. Electron Spectrosc.* **1973**, *2*, 51.

(19) Spanget-Larsen, J. *J. Electron Spectrosc.* **1974**, *3*, 369.

(20) HAM/3 results quoted in ref 14 by the authors as a private communication by L. Asbrink and E. Lindholm.

(21) von Niessen, W.; Bieri, G.; Schirmer, J.; Cederbaum, L. S. *Chem. Phys.* **1982**, *65*, 157.

are, with respect to the simple 2ph-TDA results, uniformly shifted upwards in energy by about 0.9 eV, partially because of the more accurate treatment of ground-state correlations. On the other hand, the π states are much less influenced and shifts of only $\simeq 0.3$ eV are observed for their ionization energies.

To show the influence of the polarization functions on the main ionic state energies within the OVGF and ADC(3) methods we have reported in Table II the corresponding results for the double-ζ (dz) and double-ζ plus polarization functions (dz+p) basis sets. As one can see, the n state energies are raised a little (≤ 0.2 eV) by the polarization functions. This is in line with the rather localized character (lone pair orbitals) of the corresponding orbitals. In contrast the π state energies are lowered by at least twice the average shift noticed for the n states. These non-uniform shifts in the energies of the n and π states caused by the polarization functions improve the general agreement of the OVGF and ADC(3) results with respect to the experiment and suggest also a different interpretation of the second band. In fact we obtain 12.01, 13.19, and 15.9 (for the ADC(3) calculation) eV against the experimental values of approximately 11.9–12.1, 13.5, and 15.8 eV for the π_1, π_2, and π_3 main ionic state energies, respectively. In particular for the the π_1 state we observe that the effect of the additional d- and p-type functions is that of a reduction in the corresponding ionization energy by $\simeq 0.6$ eV, while concomitantly the n_1 state energy, as before mentioned, is raised up by less than 0.2 eV only. This causes a strong reduction of the vertical energy separation (0.12 eV) between the π_1 and n_2 ionization energies with respect to that of the unpolarized ADC(3) results (0.6 eV) and yet implies an inversion of their relative ordering. The results obtained by the much simpler OVGF are very close to those of the ADC(3). Considering the size of the molecules, the agreement between theory and experiment is very good. The sequence (in increasing energy) of the lowest six main ionic states, according to our GF results, is therefore n_1, π_1, n_2, n_3, n_4, and π_2. In particular we assign on firm grounds π_1 and n_2 to the second band and thus confirm the interpretation of ref 3 and 18.

The interpretation of the bands located around 16 eV and between 16.5 and 18 eV binding energy is considerably more complicated. The latter band is broad, whereas the former one is sharp but exhibits some structure. The calculations of ref 15 already pointed to the possibility that the one-particle model of ionization may not be appropriate for these bands because in this energy region satellite lines start to acquire considerable intensity with a concomitant reduction in the intensity of the remaining ionic main states. This view is strengthened by the present more accurate ADC(3) calculations. Satellite lines originating from $3b_{1u}(n_2)$ and $3b_{2u}(n_4)$ orbitals appear already around 14.5 eV, and the third π ionic state has lost as much as 40% of its pole strength to satellite lines. Between 16 and 17.6 eV we have calculated seven satellite lines that derive from the $3b_{1u}$, $3b_{2u}$, $2b_{1u}$, $1b_{3u}$, $2b_{2u}$, and $3a_g$ ionizations. The $3a_g$ main line is also subject to a considerable reduction of its relative intensity (0.6). In contrast the ionization processes out of the $2b_{1u}$ and $2b_{2u}$ orbitals, although they give rise to many satellite lines and although their orbital energies themselves lie in an energy region where the self-energy has poles, are better interpretable in terms of the orbital model. We indeed obtain for the $2b_{1u}$ and $2b_{2u}$ main lines a relative intensity of 0.75 and 0.68, respectively.

On the basis of the present ADC(3) calculations, we thus find that for I the use of Koopmans' approximation to interpret the PE spectra above 16 eV binding energy is subject to some serious limitations. This energy region is dominated by the poles of the self-energy (two-hole one-particle excitations), and the "main" ionic states are embedded therein and have often lost considerable intensity to satellite lines. These conclusions are essentially the same as those arrived at by the 2ph-TDA results, but the present ones are much more accurate in many respects. This can be realized, e.g., by the fact that the 2ph-TDA calculation owing to a severe cutoff in the virtual MO's space predicts satellite lines only above 17 eV at variance with the present ADC(3) calculations, in which the SCF MO's space was to a large extent exhausted. The structure of the satellite lines above 16 eV appears sensitive to the polarization functions added to the basis set. In fact while the low-lying satellite lines found at 14.33 and 14.82 eV were calculated at 14.58 and 14.75 eV with the smaller basis set (dz), the satellite lines calculated around 16.2 eV (of b_{1u} and b_{3u} symmetry) lie about 1.5 eV higher in energy within the ADC(3) calculation performed with the smaller basis set. Furthermore in this latter calculation one satellite line of symmetry b_{3u} only was found up to 20 eV, at variance of the one which used the augmented basis set in which two lines of this symmetry can be seen to lie below 19 eV. It also can be observed that for all the satellite lines listed in Table I, by approaching the exhaustion of the basis set the ADC(3) results shift uniformly to lower binding energy. The broad band between 16.8 and 18 eV is, however, according to our GF results, largely dominated by the $2b_{1u}$ and $3a_g$ ionizations although two strong satellite lines of b_{3u} and b_{1u} symmetry have been calculated around 17 and 17.4 eV, respectively. Other satellite lines have been calculated with too small relative intensities and are therefore difficult to identify in the experimental spectra. For instance, the small prominence seen in the He I spectra of ref 16 between 14 and 15 eV is probably an indication of the two lowest satellite lines of symmetry $3b_{1u}$ and $3b_{2u}$ calculated in our GF results at 14.13 and 14.60 eV, respectively.

The calculations of ref 16–20 were based on the one-particle model of the ionization process and thus are of limited validity above 14 eV binding energy. ADC(3) calculations seem appropriate to correctly interpret this region of the PES of I. For highly accurate results a more refined approximation to the self-energy operator, e.g., the ADC(4) scheme,[6] is needed using even larger basis sets than used here. Such calculations for I, however, are nowdays out of range. More experimental work (other than PES) on ionic states in this energy range would also be useful.

b. Disubstituted *s*-Tetrazines. In the introduction it was mentioned that we are interested in the effects on the ionization energies and spectroscopic factors (pole strengths) brought about by substituting the hydrogen atoms of *s*-tetrazine by groups with increasing π electron-donor character like $-OCH_3$, $-SCH_3$, or $-N(CH_3)_2$. Since the ab initio GF calculations of the fully methylated compounds are costly, in particular for the latter two molecules even when double-ζ basis sets are used, we replaced the methyl groups in bis(methylthio) and bis(dimethylamino) (PE spectra thereof have been measured in ref 3) with hydrogens in our calculations. That is we attempt to simulate the theoretical PE spectra of these latter compounds by calculating the ionization spectra of the chemically closely related molecules IV and V. For these latter molecules as well as for II no experimental data on ionization energies are known to the authors. Experimental investigations are probably hampered seriously by tautomerism. To study the methyl effect on the calculated PE spectra within our theoretical and computational framework, we have also performed ADC(3) as well as OVGF calculations on III. This will allow us for III to directly compare our results with the experiments of ref 3, whereas for IV and V the comparison with experiment, after an evaluation of the methyl effect wherever appropriate, will be qualitative only.

In the low-energy valence region I shows three occupied molecular orbitals of π-type and four of n-type. The π MO's are much more sensitive than the n ones to substitutions because of their delocalization and large polarizability. This fact is already realized by looking at the experimental energy shifts, caused by methyl groups (see ref 3), which are for the π bands twice as large as those observed for the n bands. The energies of the π MO's are also much more sensitive to additional polarization functions in the used basis set than the energies of the n ones as we have seen in the previous subsection. We can easily imagine that substituents which permit a further delocalization of the π orbitals like $-OR$, $-SR$, and $-NR_2$ will influence more strongly the MO pattern of the parent molecule. The substitution of the hydrogen atoms with the electron-donating groups $-OH$, $-SH$, and $-NH_2$ leads to 21 occupied valence MO's, that is six more valence orbitals (two π and four σ) than the parent molecule. For the methoxy

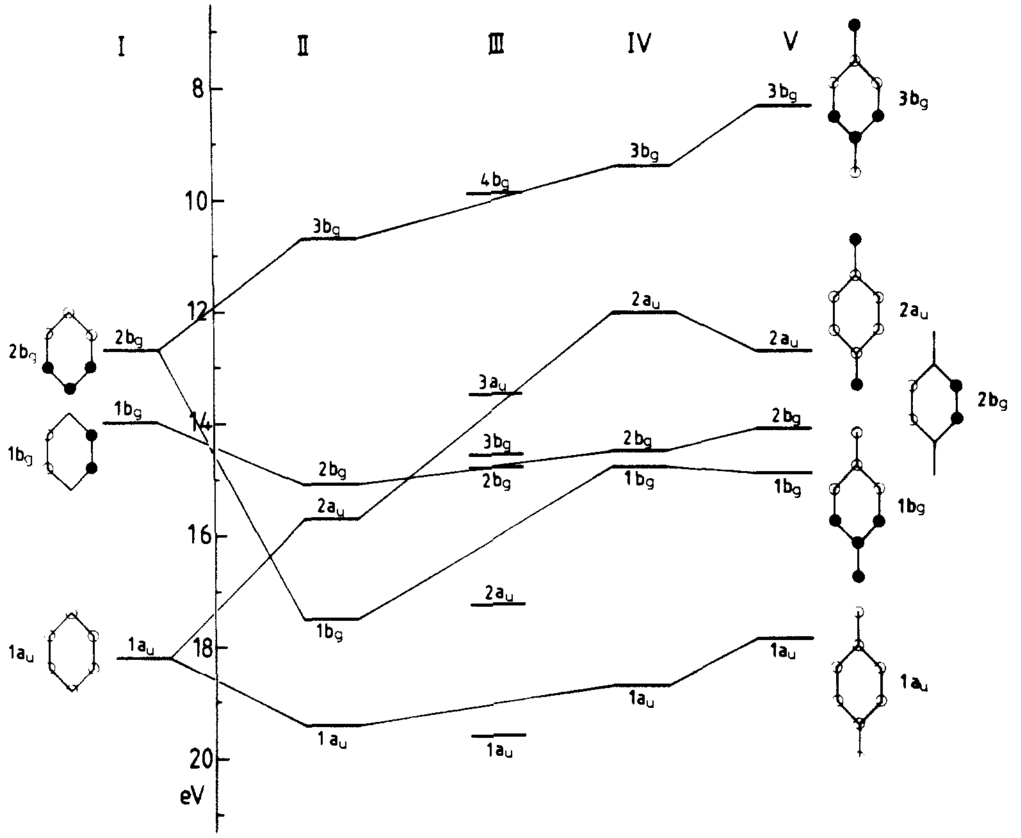

Figure 2. Correlation diagram of the π-symmetry Hartree-Fock orbital energies for *s*-tetrazine and its disubstituted compounds (double-ζ basis set calculations) studied in this work.

group we obtain instead 27 occupied valence MO's, i.e. twelve more (four π and eight σ) orbitals than *s*-tetrazine. This substitution alters the electronic structure of the *s*-tetrazine skeleton mainly in two respects. First the whole ordering in energy of the MO's is noticeably changed. Second the density of states of ionization and ionization plus excitation type is noticeably increased and they appear at lower energy. This may lead eventually to the appearance of strong many-body effects at still lower energy than already observed in the parent molecule. Finally, the two lowest unoccupied MO's of I (both π orbitals) might also be altered in their localization properties as well as in energy. This, however, is seen, a posteriori, not to be the case for the molecules investigated here.

We discuss in some detail how this rearrangement of the π MO's pattern follows by substitution of the two hydrogen atoms with the groups considered here. Among the three π MO's of I only b_{2g} and b_{3u} combine with the p orbitals of the substituent groups. The b_{1g} orbital, localized on the ring's nitrogens only, does not combine for symmetry reasons and experiences only polarization energy shifts. To illustrate the appropriate relationships between the SCF π MO's of I and those of compounds II–V a correlation diagram is reported in Figure 2. For better readability we report the π MO's of I and V within the symmetries of the C_{2h} group. It is seen from this diagram that the substitution leads to two noticeable effects on the pattern of the MO's. The first π level is pushed upwards in energy (i.e. to lower binding energy) by about 20–30% of the orbital energy of the parent molecule, and the second π orbital appears to be an a_u MO rather than a b_g one. This a_u orbital is peculiar of the substituent groups as can be seen by its localization properties, but it also has significant contributions from the ring's nitrogens. The extent of the shifts mentioned above is easily correlated with the increasing electron-donor character of the substituents along the series $-OH$, $-OCH_3$, $-SH$, and $-NH_2$. The n levels are seen not to be influenced so much by the substitutions. One consequence is that already in Koopmans' approximations we expect in the substituted *s*-tetrazines the first π band to lie now very close to the first n band. It could also be that by increasing the electron-donating character of the substituents, the π_1 band lies at lower binding energy than the n_1 band. Semiempirical hamiltonians should show this trend, and they do indeed.[3] In particular since the latter include some correlation and reorganization effects implicitly via the parameters, they could sometimes be successful in describing the ordering of those low-lying main ionic states for which a one-particle picture of the ionization applies.

For the n MO's of the substituted compounds we observe at the SCF level, in general, neither strong energy shifts with respect to the *s*-tetrazine n MO's nor the appearance at lower binding energy of MO's peculiar of the substituent groups. An exception to this trend is found in IV where the two almost degenerate MO's at about 13.8 eV ($7a_g$ and $8b_u$) are characteristic of the $-SH$ moieties and can be traced back to the lower binding energy of the 3s/3p atomic orbitals of the sulfur atom compared to those of the oxygen. The orbitals $8a_g(n_1)$, $7b_u(n_2)$, $6a_g(n_3)$, and $6b_u(n_4)$ of IV can be called lone pair orbitals. Thus the sulfur orbitals are interspersed among the n orbitals. As pointed out in ref 15 the lowest unoccupied MO's (LUMO's) of such molecules play an important role in determining the magnitude and type of correlation effects that arise in post-HF treatments of the electronic structure. Similarly they determine to a large extent the energies of low-lying excited states seen in the visible and UV electronic spectra. The two aspects of course are intimately related. We shall see, for example, that the lowest satellite lines in the PE spectra of the molecules investigated here are characterized by $\pi \rightarrow \pi^*$ excitations on top of a hole configuration such as $8a_g^{-1}$, $8b_u^{-1}$, or $3b_g^{-1}$. Similarly to *s*-tetrazine, the two LUMO's of compounds II–V are of π symmetry and have very small positive energies. In particular the first LUMO is localized on the ring's nitrogens for all molecules studied here, while the second LUMO is delocalized over the entire π skeleton. These observations should be qualitatively independent from the fact that we used for compounds II–V a double-ζ basis set.

The existence of low-lying virtual orbitals of π symmetry and of occupied π orbitals will cause, on quite general grounds, large and non-uniform many-body effects[22,23] as has been previously shown for *s*-tetrazine. Thus a one-particle approximation may

Table III. Ionization Energies (eV) and Relative Intensities of Dihydroxy-*s*-tetrazine (II) and Dimethoxy-*s*-tetrazine (III) in the Low-Energy Region

II[a]				III[b]				
orbital[c]	$-\epsilon_i$	OVGF	ADC(3)	orbital[c]	$-\epsilon_i$	OVGF	ADC(3)	exptl
n_1 $8a_g$	11.33	9.20 (0.90)	9.33 (0.88)	n_1 $10a_g$	10.68	8.76 (0.91)	9.09 (0.90)	9.05[d]
π_1 $3b_g$	10.67	10.21 (0.90)	10.30 (0.88)	π_1 $4b_g$	9.90	9.44 (0.91)	9.56 (0.91)	9.6
n_2 $8b_u$	14.68		11.96 (0.70)	n_2 $10b_u$	13.78		11.63 (0.71)	11.2
n_3 $7b_u$	16.15		{13.40 (0.20)	π_2 $3a_u$	13.56	12.25 (0.92)	12.37 (0.88)	11.8
			13.47 (0.61)	$10b_u$			12.93 (0.11)	
π_2 $2a_u$	15.66	13.70 (0.88)	13.75 (0.84)	n_4 $9b_u$	14.70		13.26 (0.82)	
n_4 $7a_g$	16.18	13.92 (0.89)	13.89 (0.84)	n_3 $9a_g$	14.53		13.32 (0.90)	
π_3 $2b_g$	15.12	14.17 (0.87)	13.94 (0.81)	$8b_u$	15.62		13.50 (0.82)	
$7b_u$			14.38 (0.08)	π_3 $3b_g$	14.61		13.65 (0.84)	
$6b_u$	17.27		15.31 (0.79)	π_4 $2b_g$	14.83		14.04 (0.90)	
$(8,6)b_u$			15.44 (0.16)	$8a_g$	16.21		14.22 (0.84)	
$6a_g$			15.65 (0.25)	$8b_u$			14.50 (0.03)	
$1b_g$	17.53	15.49 (0.88)	15.68 (0.82)	$2a_u + 3a_u$			14.89 (0.06)	
$6a_g$	18.07		15.97 (0.57)	$10b_u + 9b_u$			15.13 (0.13)	
				$2a_u$			15.57 (0.05)	
				$2a_u$	17.25		15.64 (0.59)	
				$7b_u$	17.31		16.05 (0.82)	
				$7a_g$	17.43		{16.14 (0.36)	
							16.28 (0.55)	

[a] Total SCF energy: −443.977 au. [b] Total SCF energy: −521.976 au. [c] Symmetries in the C_{2h} point group symmetry. [d] Reference 3.

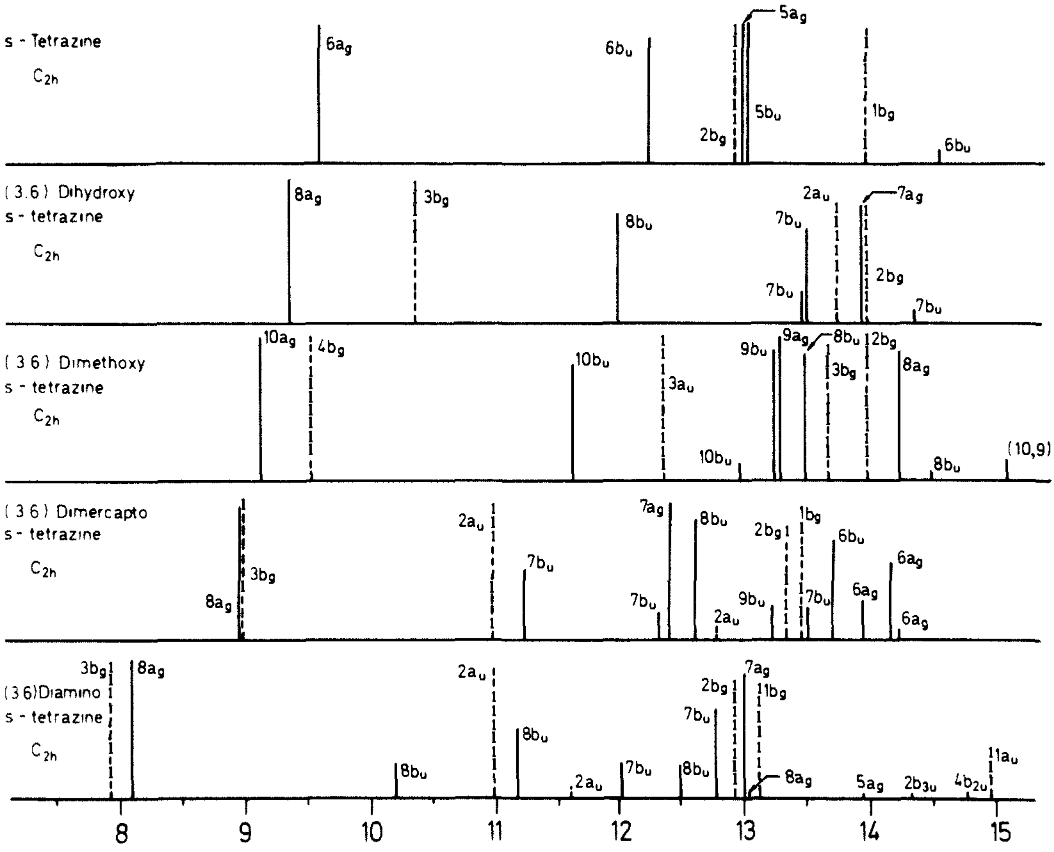

Figure 3. Schematic representation of the calculated PE spectra for *s*-tetrazine and its disubstituted compounds (ADC(3) with the double-ζ basis set calculations) investigated here. The position of the bars on the horizontal axis gives the energy (in eV) of the ionic states, while their height indicates roughly the value of the corresponding spectroscopic factors. Solid lines indicate σ-derived ionic states, while broken lines indicate π-derived main ionic states.

often be inappropriate. Correlation and relaxation effects have to be included. To calculate the ionization energies of the substituted *s*-tetrazines reliably we used the OVGF and the ADC(3) methods. In Tables III and IV we have listed the results of our GF calculations for the ionization energies as well the SCF orbital energies of the substituted *s*-tetrazines. Only ionic states with binding energy below about 15–16 eV are reported. In Figure 3 we report also the low-energy valence PE stick-spectra of *s*-tetrazine and its substituted compounds II–V as calculated by the ADC(3) method without polarization functions.

As was found for the parent molecule, the ab initio SCF approximation is to a large extent inadequate to interpret the PES of the substituted molecules. The GF methods, instead, supply for the main lines a very good and, with respect to the satellite lines structure, qualitatively reliable understanding of the various ionization processes. The ionization energies are indeed shifted on average by about 2–3 eV in the GF results because of relaxation and correlation effects. Only the first π ionic main states seem to deviate from this behavior. For them smaller corrections are observed. This is in agreement with the expectations[22,23] and

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(22) Cederbaum, L. S. *Chem. Phys. Lett.* **1974**, *25*, 562.

(23) Chong, D. P.; Herring, F. G.; McWilliams, D. *J. Electron Spectrosc.* **1975**, *7*, 445.

Table IV. Ionization Energies (eV) and Relative Intensities of Dimercapto-*s*-tetrazine (IV) and Diammino-*s*-tetrazine (V) in the Low-Energy Region

IV[c]				V[d]			
orbital[a]	$-\epsilon_1$	OVGF	ADC(3)	orbital[b]	$-\epsilon_i$	OVGF	ADC(3)[e]
n_1 $8a_g$	11.05	8.80 (0.89)	8.96 (0.84)	π_1 $2b_{2g}(3b_g)$	8.45	7.95 (0.90)	7.88 (0.87)
π_1 $3b_g$	9.38	8.77 (0.91)	9.02 (0.89)	n_1 $3b_{3g}(8a_g)$	10.07	7.97 (0.89)	8.11 (0.88)
π_2 $2a_u$	11.93	10.79 (0.90)	11.01 (0.86)	n_2 $4b_{1u}(8b_u)$	13.53		10.21 (0.21)
n_2 $7b_u$	14.40		{11.26 (0.45)	π_2 $2b_{3u}(2a_u)$	12.79		11.04 (0.81)
			12.36 (0.18)	$4b_{1u}$			11.17 (0.5)
$7a_g$	13.73	12.31 (0.90)	12.40 (0.86)	$2b_{3u}$			11.59 (0.04)
$8b_u$	13.95		12.65 (0.74)	$4b_{2u}(7b_u)$			12.05 (0.23)
$2a_u$			12.79 (0.02)	$4b_{1u}$			12.47 (0.21)
$8b_u$			13.20 (0.19)	n_3 $4b_{2u}$	15.32		12.77 (0.57)
π_3 $2b_g$	14.50		13.34 (0.73)	π_3 $1b_{1g}(2b_g)$	14.18		12.91 (0.77)
π_4 $1b_g$	14.80		13.47 (0.73)	n_4 $5a_g(7a_g)$	15.52		12.99 (0.79)
$7b_u$			13.52 (0.20)	$3b_{3g}$			13.02 (0.01)
n_4 $6b_u$	16.27		13.69 (0.67)	π_4 $1b_{2g}(1b_g)$	14.94		13.12 (0.76)
n_3 $6a_g$	15.99		{13.97 (0.23)	$5a_g$			13.85 (0.01)
			14.16 (0.52)	$2b_{3u}$			14.32 (0.01)
			14.38 (0.06)	$4b_{2u}$			14.77 (0.03)
				$1b_{3u}(1a_u)$	17.98		14.86 (0.33)

[a] Symmetries in C_{2h} point group symmetry. [b] Symmetries in D_{2h} group symmetry (symmetries in C_{2h} given in brackets). [c] Total SCF energy: −1089.0.11 au. [d] Total SCF energy: −404.374 au. [e] Results obtained with the DDA procedure and the same number (43) of virtual MO's as that used in the OVGF calculations (see section II for details).

consistent with the similar trend observed for the corresponding ionization energies of I. Both GF methods are in substantial mutual agreement with respect to the prediction of the lowest principal ionization energies, i.e. those states for which the ionization process is well described by the one-particle model. Slight differences only are observed between the OVGF and the ADC(3) results. These have been mainly caused by computational approximations (i.e. for II and IV neglection of virtual MO's). The size of these molecules hampers the full exhaustion of the basis set in the ADC(3) approximation scheme.

Inspection of the ADC(3) results shows that the one-particle model runs into strong difficulties already for the third and fourth ionization energies of compounds IV and V, respectively. We notice that the relative intensity (pole strength) of the second ionic state deriving from an n orbital is, because of correlation effects, either strongly reduced or the corresponding line is broken up into two or more components. This effect, which is herein observed systematically for all of the substituted *s*-tetrazines but not for the corresponding ionic state of the parent molecule, must be related to the changes on the MO's of the ring caused by the substituents. In particular the second n ionization, n_2, energies are severely affected by correlation effects. This splitting or strong reduction of the intensity may well be the origin of the small intensity, which can be associated to the n_2 bands in the experimental PE spectra of ref 3 for bis(methylthio) and bis(dimethylamino) *s*-tetrazine. In fact as mentioned in the introduction, it is quite difficult to identify and to assign the second n band in the existing experimental PE spectra of these latter molecules as well as for similar *s*-tetrazines with strong electron-donor groups.

Another interesting aspect of the present results is the phenomenon of the hole-mixing[21] which appears in the substituted *s*-tetrazines but not in the parent molecule. This phenomenon is an effect of the correlations among electrons. Although in first order single-hole configurations within the HF approximation do not couple, they can indirectly couple at higher order through one or several poles of the self-energy. Depending on the strength of these couplings the relative intensity of a given line may arise from two or more orbitals of the same symmetry. However, the occurrence of this phenomenon for one or more orbitals does not mean by itself that the orbital model of the ionization process fails. Rather its appearance depends on the details of the reference mean field. By performing an appropriate unitary transformation of the occupied (and separately of the unoccupied) canonical HF orbitals and by carrying out the same GF calculation with the transformed orbitals, we would not encounter any hole-mixing phenomenon. Within the Hartree–Fock reference state it however appears as a genuine effect of the electron–electron correlation. We shall briefly comment on this aspect of our results below. All of these new features appearing in the calculated PE spectra of II–V are probably related to the increased density of states in the low-energy valence region, which enhances the importance of correlation effects.

As we mentioned above the ordering and the symmetry characterization of the first two main ionic states is of considerable interest in this series of molecules. Our results indicate that on going from II to V, i.e. by increasing the electron-donor character of the substituent, the inversion of the n_1 and π_1 bands takes place. We can observe this effect already in IV where the n_1 and π_1 states are almost degenerate, in contrast to II and III where they are separated by about 1 and 0.5 eV, respectively. Since these outermost ionization energies derive from the corresponding n_1 and π_1 states of *s*-tetrazine for which we studied the effect of the polarization functions we can argue that these latter functions added to the basis set should bring about a slight raise and a noticeable lowering of the n_1 and π_1 ionization energies, respectively. In this respect the very good agreement in comparison with the experiment (see Table III) of the first two ionization energies is probably, at least in part, due to a compensation of the basis set errors with the ones caused by the truncation of the virtual MO's space (see section II). We notice that a methyl group in the substituent moiety enhances its electron-donor character, i.e. it lowers the π states more than the n ones (compare II and III). If one considers this effect on our ADC(3) or OVGF results for IV and if one takes into account the shift due to polarization functions the energy of the π_1 and n_1 bands can be set to about 8.5 and 9.2 eV, respectively. The agreement with respect to the assignments of the experimental bands of methyldimercapto-*s*-tetrazine proposed in ref 3 seems thus quite satisfactory. In V the π_1 and the n_1 band after consideration of the methyl and polarization functions effects would seem to be calculated too low (≃7.5 and 8.1 eV) with respect to the experimental data on methyldiamino-*s*-tetrazine of ref 3. However, a different behavior of these effects in V cannot be excluded.

As to the ionizations deriving from the n_2 and π_2 MO's, it was mentioned before that the experimental PE spectra of the methylated derivatives of IV and V do not show bands which could unequivocally be associated with them. For the methyldimercapto-*s*-tetrazine the sharp band at about 9.8 eV and the broad weak structure at 10.4 eV were assigned in ref 3 to the π_2 and n_2 main ionic states, whereas for methyldiamino-*s*-tetrazine the n_2 ionic state was assigned to the structures at the high energy side of the peak at 9.3 eV (π_2). Anyway it seems clear that the spectra indicate a surprisingly too low intensity of the n_2 ionic state. These experimental facts can be well explained within our ADC(3) results. The ordering in increasing energy of these two states, according to Gleiter et al., should in the disubstituted tetrazines with strong electron-donor groups still be π_2, n_2. Inspecting the ADC(3) results for IV we observe in fact that the third ionic state is of π symmetry, i.e. the π_2. By taking into account an energy shift for the methyl groups of about 0.5 eV and a shift of roughly the same amount for the polarization functions, we could set the energy of this state roughly around 10.0 eV, which should be compared with the experimental value of ca. 9.8 eV. The $7b_u$ (n_2) ionization energy is calculated for non-methylated compound IV at about 11.3 eV, which has to be compared with the experimental value of 10.4 eV for the methylated compound. The shifts due to the methyl group and due to polarization functions are rather difficult to estimate for the n_2 state. The conclusion drawn from the data for II and III in Table III is not transferable to the present case, since the n_2 is only one component of the $7b_u$ ionization and such a failure of the orbital picture of ionization can be sensitive to substitutions and the inclusion of polarization functions.

We would like to stress here the selectivity of the many-body effect occurring for the two outermost b_u ($8b_u$, $7b_u$) orbitals of IV. In fact we expect for the $7b_u(n_2)$ ionization strong correlation effects since it corresponds to that of the $6b_u$ of I where a shift of 2 eV (2.5 eV for the double-ζ basis set) for the energy was observed (see Tables I and II), whereas for $8b_u$ as well as for the $7a_g$ ionizations the correlation effects are not expected to be so strong because these orbitals are dominated by contributions of the sulfur atomic orbitals. This dependence of the many-body effects on the localization character of the orbitals of the same symmetry may cause an inversion of the ordering from that provided by Koopmans' approximation. We observe indeed a shift of about 3.2 eV for the $7b_u$ orbital energy and the splitting of the main line intensity into several components, whereas for $8b_u$ this shift is about 1.3 eV and no splitting is observed.

It is with difficulty that the same rationale may be applied to the results of V. To estimate the shift on the ionization energies due to the methyl group for this molecule is even more difficult than for the previous case. The ionization from the n_2 ($4b_{1u}$) orbital gives rise to three strong components, according to the ADC(3) results, showing thus a complete failure of the molecular orbital model for this ionization process.[24] We notice also that the π_2 line and the strongest component of the n_2 line are almost degenerate. Severe splitting of the intensity for the ionization from the n_2 orbital in IV and for ionization out of the n_3 orbital in II and III also takes place. This breakdown of the molecular orbital model for the ionization out of the n_2 orbital in IV and V may well explain the difficulties encountered with the methylated derivatives in identifying the n_2 states. However, according to our results, we suggest that for the bis(dimethylamino)-*s*-tetrazine, the band seen in the experiment around 9.4 eV should contain the π_2 line and one component of the n_2 lines, although the accuracy of the absolute energies calculated here is somewhat limited, because of the lack of polarization functions.

In the following section we discuss the microscopic origin of the effects that cause the splitting of the low-lying n_2 lines in IV and V. Orbitals in the inner valence energy region also exhibit similar phenomena,[24] but for the outer valence orbitals this is quite unusual.

To understand why some low-lying lines split and others do not, we have to look at the lowest poles of the self-energy matrix. Within the theoretical scheme used here these poles arise mainly from 2h1p configurations, i.e. particle-hole excitations of ionic configurations. For our purpose we consider only the B_u and A_u symmetries of the C_{2h} point-group symmetry. We begin with the B_u symmetry. The leading configurations in the self-energy poles can uniformly be described as $\pi \rightarrow \pi^*$ excitation on top of an n-hole (or, equivalently, as $n \rightarrow \pi^*$ excitation on top of a π-hole) configuration. These 2h1p configurations do not involve b_u orbitals and in this respect they are correlation shake-ups.[24] We also note that these 2h1p configurations couple simultaneously with more than one b_u^{-1} configuration although not with the same strength, and we thus encounter here a weak hole-mixing effect.[21] The trend in energy of these 2h1p configurations on going from I to V is relevant for the appearance of strong correlation phenomena at low ionization energies (see next chapter).

As to the A_u symmetry species we notice that for I to III there are no low-lying poles of the self-energy in our ADC(3) calculations which couple with the lowest energy a_u^{-1} hole configurations, whereas for V and for IV we have 2h1p configurations at 11.85 and 12.63 eV, respectively, which couple, however, very weakly. This finding on the self-energy poles within the A_u symmetry is fully consistent with the fact that in this symmetry there appear no satellite lines with noticeable relative intensity of this symmetry in the calculated ADC(3) ionization spectra for molecules I–V (see Tables I, III, and IV). This fact makes Koopmans' approximation for the first π ionic state quite reliable and applicable for the molecules studied in this work as well as for the closely related molecular system investigated by Gleiter et al. in ref 3.

IV. Discussion of Low-Lying Satellite States

One of the most significant results of this work is the appearance of very low lying non-Koopmans correlation satellite states in compound V. We attempt here a discussion of their origin in simple terms. This may be helpful in undertaking a systematic search for other systems exhibiting the phenomenon. In systems of the type discussed here the $\pi \rightarrow \pi^*$ excitation from the highest occupied π orbital to the lowest unoccupied π^* orbital is usually connected with the smallest excitation energy in the parent neutral molecule. To first order this excitation energy $\Delta(\pi\rightarrow\pi^*)$ is given by (triplet excited state)

$$\Delta(\pi\rightarrow\pi^*) = \epsilon_{\pi^*} - \epsilon_{\pi} - J_{\pi\pi^*} \qquad (1)$$

where $J_{\pi\pi^*}$ is the usual Coulomb integral. For *s*-tetrazine (I) and V obtained by disubstitution we obtain

$$\Delta(\pi\rightarrow\pi^*) = \begin{cases} 4.8 \text{ eV} & \text{for I} \\ 2.8 \text{ eV} & \text{for V} \end{cases}$$

The excitation energy is thus substantially lowered by adding the electron-donor substituent. The reason for this lowering is mainly due to the change in ϵ_π as indicated in Figure 2.

In the next step we consider the $\pi \rightarrow \pi^*$ excitation energy in the ion. Since the π orbital is involved in the excitation, we consider the next highest occupied orbital, i.e., the n_1 orbital, to be the orbital out of which the ionization takes place. The $\pi \rightarrow \pi^*$ excitation energy $\Delta_n(\pi\rightarrow\pi^*)$ in the presence of a hole in the n_1 orbital is, in first order, given by[25]

$$\Delta_n(\pi\rightarrow\pi^*) = \Delta(\pi\rightarrow\pi^*) + (J_{n\pi} + \tfrac{1}{2}K_{n\pi}) - (J_{n\pi^*} - \tfrac{3}{2}K_{n\pi^*}) \qquad (2)$$

where $K_{n\pi}$ and $K_{n\pi^*}$ are the common exchange integrals. We note that in I the n_1 orbital is actually the HOMO and in V it is the second HOMO. The excitation energies in the ions are easily determined from (2) and read

$$\Delta_n(\pi\rightarrow\pi^*) = \begin{cases} 4.7 \text{ eV} & \text{for I} \\ 1.7 \text{ eV} & \text{for V} \end{cases}$$

Whereas the $\pi \rightarrow \pi^*$ excitation energy in I is hardly changed due to ionization, it is clearly lowered in V. This finding is easily understood. The orbitals n_1 and π^* are localized on the rings' nitrogens and do not change markedly upon disubstitution. Indeed we find $J_{n\pi^*} - {}^3/_2K_{n\pi^*}$ to be 8.2 eV in I and 8.0 eV in V. The π orbital, on the other hand, changes substantially upon disubstitution and is delocalized over the whole molecule. This leads to a lowering of the Coulomb interaction between the charge distributions in π and n_1. Here we find $J_{n\pi} + {}^1/_2K_{n\pi}$ to be 8.1 eV for I which changes to 6.9 eV upon disubstitution. By creating a hole in n_1 there is a charge transfer from the substituents to the rings' nitrogens as indicated by the $\pi \rightarrow \pi^*$ excitation. This relatively efficient screening[25] of the hole, which is absent in I,

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(24) Cederbaum, L. S.; Domcke, W.; Schirmer, J.; von Niessen, W. *Adv. Chem. Phys.* **1986**, *65*, 115.

(25) Schirmer, J.; Angonoa, G.; Cederbaum, L. S. *Z. Phys. D* **1987**, *5*, 253. Domcke, W.; Cederbaum, L. S.; Schirmer, J.; von Niessen, W. *Chem. Phys.* **1979**, *39*, 149.

leads to the lowering of the excitation energy in the cation of V.

Let us turn to the satellite state(s). For a low-lying satellite state to be visible in the spectrum its binding energy must be small and its coupling to a Koopmans' state substantial. The binding energy of the state where an electron is ejected from the n_1 orbital and another one is excited from the π_1 to π^* orbital is, again in first order, given by adding $-\epsilon_{n_1}$ to the excitation energy in the ion $\Delta_n(\pi \rightarrow \pi^*)$. We find

$$-\epsilon_{n_1} + \Delta_{n_1}(\pi \rightarrow \pi^*) = \begin{cases} 16.2 \text{ eV} & \text{for I} \\ 11.8 \text{ eV} & \text{for V} \end{cases}$$

Interestingly, this satellite state is of B_u symmetry and cannot couple to the Koopmans's state n_1 which is of A_g symmetry. It does couple, however, to the n_2 Koopmans' state. This coupling is substantial in both I and V since the coupling integrals $V_{n_2\pi^*n_1\pi}$ involve orbitals all exhibiting considerable contributions in the same region of space ($V_{n_2\pi^*n_1\pi}$ is 2.2 eV for I and 2.0 for V). Note that the ionization energy on Koopmans' level $-\epsilon_{n_2}$ is 13.5 eV for V (14.5 eV for I) and lies well above the binding energy of 11.8 eV of the satellite. The interaction between the two corresponding states will thus further push down the energy of the satellite state. We see that the appearance of a very low lying satellite state due to substitution can be explained using only the Hartree–Fock orbitals of the neutral species and simple first-order theory.

V. Concluding Remarks

In this work we have addressed problems related to the interpretation of the low-energy bands in the PE spectra of some disubstituted *s*-tetrazines as well as of their parent molecular system. These problems have the typical facets which one encounters in understanding a PES, i.e. the ordering and the orbital origin of the first few low-energy ionic states, and the difficulties in identifying some bands that are expected to appear in the spectra on grounds of simple arguments. It has become clear over the last 10 years that these two aspects of our attitude to look at the PE spectra correspond to the two fundamental aspects of the usual electronic Hamiltonian, that is the one-particle operator (e.g. the Hartree–Fock) and the many-body effects. Although it was long known that the many-body part of the Hamiltonian tunes the one-particle part behavior of it, so that for example the Koopmans' approximation to the ionization processes needs refinements because of relaxation and correlation effects, it turned out that the importance of these latter effects, often, is such that the concept of one-particle operator can be blurred and may loose thus its physical meaning and utility. Within our GF calculations on the molecular systems studied in this paper, we have observed this phenomenon for the third ionic main state of π symmetry (π_3) of *s*-tetrazine and in a dramatic way for the second n (n_2) bands (i.e. at very low energy, $\simeq 11.0$ eV) of the dimercapto- and diamino-*s*-tetrazines. We have correlated the occurrence of this phenomenon, which does not occur for the n_2 band of the other closely related molecules, to the energy shifts on the orbital energies brought about by the strong electron-donor character of the substituents. This phenomenon, which leads to a severe limitation of the one-particle model of the ionization, is very probably the origin of the difficulties encountered for the identification of the n_2 bands in the experimental spectrum. These effects are responsible for the relative ordering of the n_1 and π_1 bands in the disubstituted *s*-tetrazines. The latter band is indeed more and more pushed to lower energy by increasing the electron-donor capacity of the substituent until it preceds the n_1 band. The ordering (g, u, g, u) of the n orbitals of the *s*-tetrazine, with respect their parity, deriving from the ring's lone-pair orbitals, may also change upon substitution. Indeed we have found g, u, u, g in the substituted compounds. Wherever a direct comparison between our results and the experiment was possible (see Table I for I and Table III for III) we find a very satisfactory agreement which gives us confidence on the reliability of the observations and suggestions discussed in this work.

We have calculated, within the ADC(3) method, ionic states up to about 22 eV, and presented only those up to about 16 eV (18 eV for *s*-tetrazine). Therefore a few remarks on the inner valence PE spectra may be appropriate for the sake of completeness. Between 16 and 22 eV compounds II–V exhibit in the calculated PE spectra a smearing out of the spectral intensity over many satellite lines, which derive mostly from inner valence ionizations, for which generally a failure of the one-electron model of the ionization processes is observed.[24] It turns out to be difficult in this energy range to identify, according to the calculated PE spectra, an ionic state that could be associated to the parent Koopmans' (main) ionic state. The large majority of the ionic states show small relative intensity (less than 0.05), whereas for some of them the calculated relative intensity may be up to $\simeq 0.3$. At yet higher energies (≥ 22 eV) similar trends of the calculated PE spectra are expected.

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