THEORETICAL INVESTIGATION

OF PHOTOELECTRON SPECTRA

OF FURAN, PYRROLE, THIOPHENE,

AND SELENOLE

A. B. Trofimov[1,2], I. L. Zaitseva[1,3],

T. E. Moskovskaya[1], and N. M. Vitkovskaya[1]

The ionization spectra of furan, pyrrole, thiophene, and selenophene have been calculated within the framework of the nonempirical quantum-chemical method with the Green's one-particle function in the approximation of the third order algebraic diagram construction [ADC(3)]. The calculated energies and the intensity of vertical transitions pertaining to the ionization of outer and inner shells are compared with the newest experimental data. The good agreement of theoretical and experimental results enabled a detailed assignment and interpretation of the observed photoelectron spectra to be carried out. Problems of disturbing the picture of orbital ionization are considered; the mechanism of formation of low-lying photoelectron satellites is explained. Certain general rules and trends of the behavior of the spectra of the systems studied are considered.

Keywords: pyrrole, selenophene, thiophene, furan, ionization, Green's function method, nonempirical quantum-chemical calculations, photoelectron spectra.

Furan, pyrrole, and thiophene are fundamental representatives of the class of five-membered heteroaromatic compounds. These key molecules play an exceptionally important role in many areas of contemporary chemistry, biochemistry, and technology. Their structural units enter into various natural products and biologically active substances, and their derivatives are building blocks for the synthesis of complex heteroatomic molecules and the making of conducting polymers [1-6].

The ionization spectra of furan, pyrrole, and thiophene serve as one of the most important sources of information on the electronic structure of these systems, in connection with which they frequently become the subject of various experimental investigations, the results of which are reflected in information publications [7-9] and review papers [10-14].

_____

* Dedicated to Academician of the Russian Academy of Sciences B. A. Trofimov on his 70th jubilee.

Previous works, carried out using He I and He II sources of excitation, were mainly devoted to outer valence ionization spectra [15-19]. In these studies cationic states low-lying in energy of the systems being considered were characterized, and also data were obtained on the vibrational structure of the corresponding photoelectron bands. Study of the angular distributions for establishing the symmetry of final states in the spectra of furan, pyrrole, and thiophene were carried out in [20-24]. It is also necessary to mention studies concerning Penning ionization [25, 26] and electron impulse (*e*, 2*e*) spectroscopy [27].

The photoelectron spectra of furan, pyrrole, thiophene [28], selenophene [29], and halogen-substituted thiophenes [30-32], obtained using the newest sources of monochromatic synchrotron radiation, characterize the most up-to-date level of spectroscopic investigations. The spectral range also includes the inner valence region, and the variation in activation energy makes possible the study of ionization dynamics.

The increase in volume and complication of spectroscopic information available in such form entails the necessity of applying theoretical approaches for the interpretation of the results of observations. Difficulties noted in this are caused by the sharp increase in the number of transitions with energy greater than 15-18 eV, and also by the disturbance of the orbital picture of ionization in this region. We recall that the latter effect consists of a displacement of spectral intensity from the main "one-hole" cationic states to a closely-lying photoelectron satellite [33]. In essence the effect is a display of multielectron interactions, linked with the ionization processes, and may only be described using theoretical methods adequately taking the effects of electron correlation into consideration.

Theoretical investigations of the ionization of furan, pyrrole, and thiophene have a long history [19, 28, 34-37]. Regretably, the significant drawback of many of the listed works, including the recent [28, 37], is, in our view, that they focus predominantly on the outer valence transitions. In addition, the consequent calculations frequently only repeat the previous at a somewhat more precise level, introducing comparatively little new to the understanding of the nature of the spectra. In the majority of cases, within the limits of discussion, transitions are found pertaining to the inner valence range, and also low-lying photoelectron satellites, the nature of which are of significant interest. Up to the present time there is a practically complete absence of attempts to clarify general rules for the spectra of the molecules considered, which all belong to one class.

The investigation undertaken by us in the present work to a certain degree closes the existing gaps in the theoretical study of the problems of ionization of five-membered heterocycles. Furthermore, the systematic calculation of photoelectron spectra of pyrrole, furan, thiophene, and selenophene is able to stimulate a reliable interpretation and most complete assignment of the photoelectron spectra of these systems [28-30]. These were carried out by us within the limits of a single approach based on the theory of Green's one-particle functions [38-40].

Description of the Approach. The energies and intensities of the vertical transitions in the ionization spectra of furan, pyrrole, thiophene, and selenophene were calculated in the third order algebraic diagram construction approach [ADC(3)] for one-particle Green functions [38-40], which has recommended itself well in similar calculations (see for example [38, 29-32, 41-43]). The ADC(3) method sequentially calculates all the main effects linked with ionization (electron correlation and orbital relaxation) and permits calculation of energies (E) and relative intensities (P) of transitions directly, avoiding separate calculation of the ground and final states.

The final cationic states here are treated in terms of configurations of the "hole" (*h*) and "two-holes-one-particle" (2*h*-1*p*) type which permits description of both the main lines in the spectrum, and in satellites, and also the situation with disturbance of the orbital picture of ionization prevailing in the inner valence regions of the spectra. The ADC(3) method is characterized by a mean error of calculation of the energies of the main photoelectron lines of ~0.2 eV (the precision for 2*h*-1*p* satellites is lower) and comparatively small calculation consumption, which makes it a fairly reliable and practical instrument for studying the ionization spectra of a wide circle of molecular systems.

For comparison calculations were also carried out by the simpler method of outer valence Green functions (OVGF) [38], which describe in third order theory disturbances of the energies and intensities of the main photoelectron transitions, but not the more energy-consuming, the final states of which have a complex multi-configurational character.

Equilibrium molecular geometries of the ground state were optimized within the framework of Mőller-Plesset second order perturbation theory (MP2) using basis sets 6-31G* [44-47]. Calculations by the ADC(3) and OVGF methods were carried out in the 6-311G* three-exponential basis sets [44-49], supplemented by polarization functions (in all cases 6-component representation of basis d-functions were used). In the ADC(3) approach orbitals of the K and L shells were "frozen", and orbitals of the selenium M shells were excluded from the calculation of selenophene by the OVGF method.

The described method, in our view, is theoretically more adequate compared with the approach using experimental geometry. In particular it enables direct comparison of the results for different molecules, which is especially important in the case of the analysis carried out in the study.

Calculations by the ADC(3) method were carried out with the aid of the AGAMIP program [50], having an interface with the standard quantum-chemical GAMESS set of programs [51]. Optimization of the geometry within the MP2 scheme and calculations in the OVGF approach were carried out using GAUSSIAN programs [52].

The envelope of the theoretical photoelectron spectra was constructed with a package of calculated spectra with functions of the gaussian type, having line halfwidth of 0.5 eV (FWHM), introduced to compensate roughly for vibrational structures and other factors not taken into account in the calculations.

General Characteristics of Ionization Spectra. The Hartree-Fock valence electron configurations for the furan, pyrrole, thiophene, and selenophene molecules in the ground state $^1A_1$ after deduction of orbitals of the inner K, L, and M shells may be recorded in the following way:

inner valence portion – $1a_1^2\,2a_1^2\,1b_2^2\,2b_2^2\,3a_1^2$;

outer valence portion – $4a_1^2\,1b_1(\pi_1)^2\,3b_2^2\,4b_2\,^2 5a_1\,^2 6a_1\,^2 2b_1(\pi_2)\,1a_2(\pi_3)^2$,

where the order of the molecular orbitals (MO) is shown for furan and may differ somewhat for other molecules.

TABLE 1. Mulliken Populations on Atoms in Molecules of Five-Membered Heterocycles for Outer Valence MO (HF/6-311G*)*

Atom	Molecular orbitals						
	$1b_1(\pi_1)$	$3b_2$	$4b_2$	$5a_1$	$6a_1$	$2b_1(\pi_2)$	$1a_2(\pi_3)$
	Furan						
O	1.29	0.46	0.01	0.67	0.46	0.45	0.01
C_α	0.27	0.41	0.28	0.04	0.25	0.09	0.69
C_β	0.09	0.07	0.41	0.43	0.43	0.69	0.31
	Pyrrole						
N	1.00	0.41	0.07	0.36	0.01	0.63	0.01
C_α	0.34	0.48	0.24	0.16	0.19	0.03	0.71
C_β	0.16	0.02	0.44	0.39	0.63	0.65	0.29
	Thiophene						
S	0.56	0.01	0.43	0.04	1.25	1.08	0.02
C_α	0.11	0.30	0.40	0.56	0.08	0.01	0.72
C_β	0.48	0.39	0.39	0.24	0.24	0.45	0.27
	Selenophene						
Se	0.43	0.01	0.56	0.04	1.25	1.30	0.00
C_α	0.39	0.39	0.48	0.24	0.24	0.01	0.72
C_β	0.40	0.30	0.11	0.56	0.08	0.34	0.28

_____

* Sum of populations of each MO (including omission of hydrogen atoms in the Table) is equal to 2.

In all the molecules considered the π-system includes three occupied MO $1b_1(\pi_1)$, $2b_1(\pi_2)$, $1a_2(\pi_3)$ and two vacant MO $b_1(\pi_4^*)$ and $a_2(\pi_5^*)$. The most deeply lying orbital $1b_1(\pi_1)$ is a bonding combination of p-orbitals of all the ring atoms with a significant contribution from the heteroatom. The MO $1a_2(\pi_3)$ describes the bond between the C_α and C_β atoms, and the MO $2b_1(\pi_2)$ from its origin may be assigned to the unshared electron pair of the heteroatom. The vacant MO $b_1(\pi_4^*)$ and $a_2(\pi_5^*)$ may be considered as antibonding in relation to MO $1b_1(\pi_1)$ and $1a_2(\pi_3)$ respectively. The localization properties of the considered orbitals reflect to a definite degree the results of calculations of the atomic populations (Table 1).

TABLE 2. Calculated (HF, OVGF, ADC(3)/6-311G*) and Experimental Energies (E) and Intensities (P) of the Main Vertical Transitions in the Outer Valence Ionization Spectrum of Furan, Pyrrole, Thiophene, and Selenophene

MO	E, eV	E, eV	P	E, eV	P	E, eV
	HF	OVGF		ADC(3)		Experiment*
			Furan			
$1a_2(\pi_3)$	8.6	8.61	0.91	8.7	0.90	9.0
$2b_1(\pi_2)$	10.8	10.0	0.90	10.2	0.89	10.4
$6a_1$	14.7	13.1	0.91	13.3	0.90	13.0
$5a_1$	15.2	13.8	0.91	14.0	0.90	12.6
$4b_2$	15.6	14.0	0.91	14.3	0.90	14.2
$3b_2$	16.5	15.1	0.90	15.2	0.89	15.2
$1b_1(\pi_1)$	17.1	15.0	0.82	15.5	0.70	15.6
$4a_1$	20.0			18.0	0.78	17.5
			Pyrrole			
$1a_2(\pi_3)$	8.1	7.9	0.91	8.1	0.89	8.3
$2b_1(\pi_2)$	9.3	8.7	0.90	8.8	0.89	9.3
$6a_1$	14.2	12.7	0.90	13.0	0.90	12.8
$1b_1(\pi_1)$	15.4	13.3	0.82	13.0, 16.6	0.40, 0.10	12.8
$4b_2$	15.0	13.2	0.91	13.6	0.90	13.6
$3b_2$	15.8	14.3	0.90	14.5	0.90	14.3
$5a_1$	16.2	14.4	0.90	14.8	0.90	15.0
$4a_1$	20.1	17.8	0.85	17.9	0.56	17.9
			Thiophene			
$1a_2(\pi_3)$	8.8	8.6	0.90	8.7	0.88	9.0
$2b_1(\pi_2)$	9.4	9.0	0.91	9.0	0.90	9.5
$6a_1$	12.9	11.9	0.90	11.9	0.90	12.1
$1b_1(\pi_1)$	14.2	12.6	0.84	12.4, 15.6	0.57, 0.13	12.5, 15.6
$4b_2$	14.4	13.1	0.90	13.3	0.90	13.3
$5a_1$	15.0	13.2	0.90	13.6	0.89	13.7
$3b_2$	15.6	13.9	0.90	14.2	0.89	14.2
$4a_1$				17.0	0.74	16.6
			Selenophene			
$2b_1(\pi_2)$	9.0	8.7	0.91	8.7	0.90	9.0
$1a_2(\pi_3)$	8.8	8.6	0.90	8.7	0.87	9.1
$6a_1$	12.3	11.4	0.90	11.5	0.90	11.7
$1b_1(\pi_1)$	13.6	12.2	0.84	12.1, 14.7	0.59, 0.16	12.1
$4b_2$	13.6	12.4	0.90	12.6	0.89	12.9
$5a_1$	15.1	13.2	0.89	13.6	0.89	13.5
$3b_2$	15.7	13.8	0.89	14.1	0.87	14.2
$4a_1$	18.8	16.7	0.85	16.6	0.38	16.5

*For furan, pyrrole, and thiophene values were obtained from the spectra given in [28], for selenophene from the data of [29].

The spectra of furan, thiophene, selenophene, and pyrrole calculated by the ADC(3) method are compared with the experimental data in Figs. 1-4 [28, 29]. The results, referring to the outer-valence region of the spectrum, are analyzed in more detail in Table 2.

As is seen from the results presented (Table 2), the mean error calculated in the ADC(3) approach for the lower vertical ionization energies relative to the experimental data was ~0.2 eV, and the maximum did not exceed 0.5 eV. For the transitions considered the results of the ADC(3) and OVGF methods were in good agreement with one another, but the mean error on using OVGF relative to the experiment was only a little greater than in the case of ADC(3). Both methods provide an appreciable improvement of results in comparison with the HF method (Koopman's theorem).
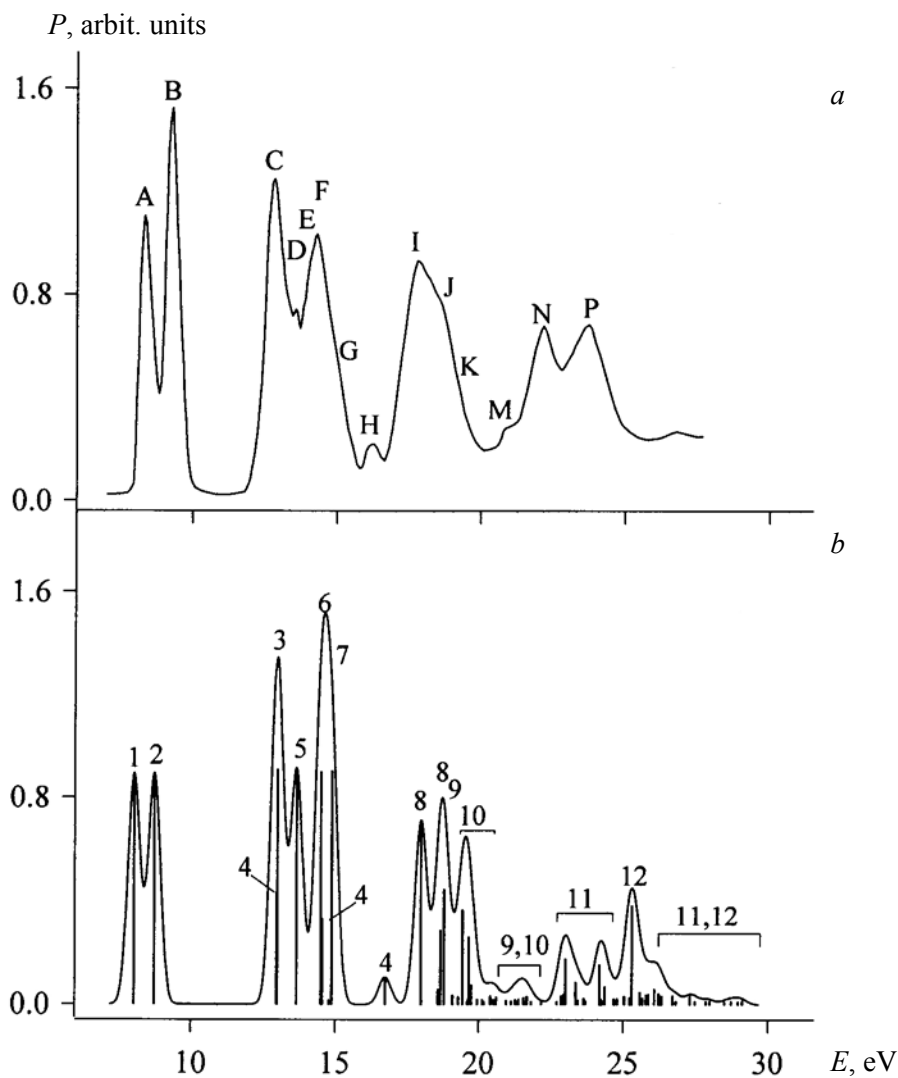

Fig. 1. Photoelectron spectra of furan: a – experimental [28] ($h\nu = 90$ eV); b – theoretical [ADC(3)/6-311G*]: $1 - 1a_2(\pi_3)$; $2 - 2b_1(\pi_2)$; $3 - 6a_1$; $4 - 5a_1$, $5 - 4b_2$, $6 - 3b_2$, $7 - 1b_1(\pi_1)$; $8 - 4a_1$, $9 - 3a_1$, $10 - 2b_2$, $11 - 1b_2$, $12 - 2a_1$.
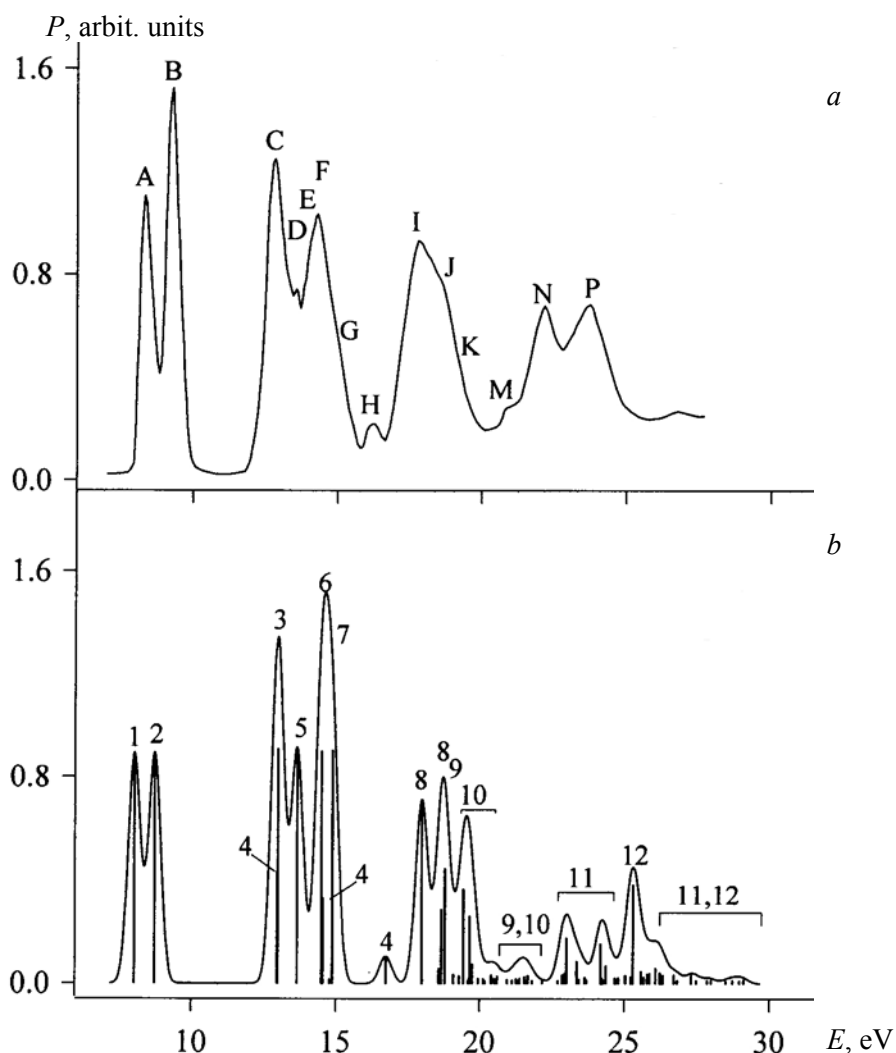
Fig. 2. Photoelectron spectra of pyrrole: *a* – experimental [28] ($h\nu = 90$ eV);
b – theoretical [(ADC(3)/6-311G*): $1 - 1a_2(\pi_3)$; $2 - 2b_1(\pi_2)$; $3 - 6a_1$; $4 - 1b_1(\pi_1)$;
$5 - 4b_2$, $6 - 3b_2$, $7 - 5a_1$; $8 - 4a_1$, $9 - 2b_2$, $10 - 3a_1$, $11 - 1b_2$, $12 - 2a_1$.

As follows from the calculated intensities of the main photoelectron lines under consideration ($P \sim 0.9$-0.8), the overall importance of the satellites is insignificant and the orbital picture of ionization is satisfied to a good approximation in the whole outer valence region. One of the exceptions is MO $4a_1$, for which a small drop in intensity is observed in furan and thiophene ($P = 0.78$ and 0.74 respectively) and a more significant drop in selenophene and pyrrole ($P = 0.38$ and 0.56 respectively). The fall in intensity of the main line $4a_1$ is accompanied by the appearance in the spectrum of attendant satellites, well marked in the theoretical spectra in Figs. 1 and 3. Another significant deviation from the orbital picture of ionization in the outer valence region is the drop for all the considered molecules in the intensity of the $1b_1(\pi_1)^{-1}$ transition ($0.4 \leq P \leq 0.7$) and the appearance linked with MO $1b_1(\pi_1)$ of "shake-up" (in the case of furan of "shake-down" also) satellites in regions of the spectrum adjacent to the main line.

In the higher energy portion of the spectrum catching the upper outer-valence range and all the inner-valence range the orbital ionization picture is rearranged which makes impossible the correlation of transitions with the ionization of individual orbitals. In this case only a dense structure of satellite lines is observed in the

1106

spectrum, reflecting the complex reorganization processes and effects of configurational interaction characteristic of this energy region. Above 15 eV in the ionization spectrum of the considered five-membered heterocycles transitions with configurations of the final state of $2h$-$1p$ begin to predominate, forming overlapping clusters of satellite lines of low intensity in place of the expected appearance of lines of the ionization of inner-valence orbitals.
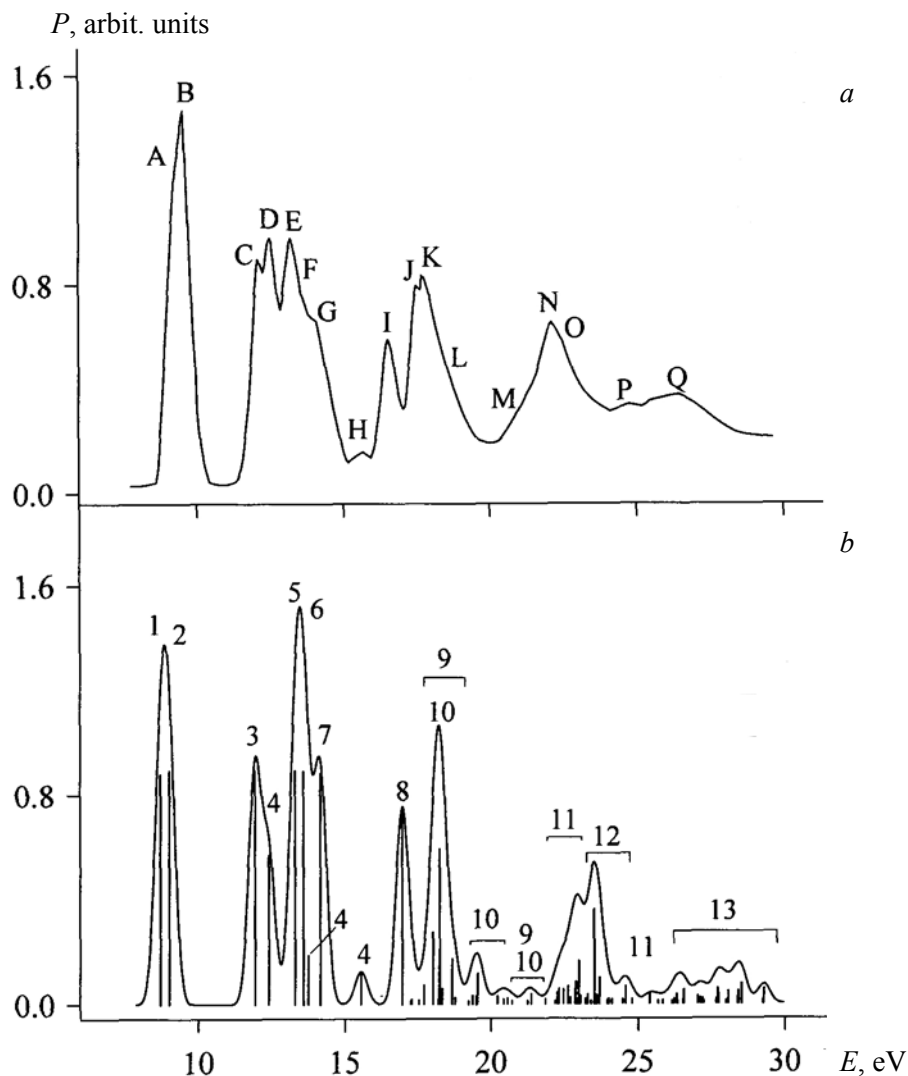

Fig. 3. Photoelectron spectra of thiophene: a – experimental [28] ($h\nu = 90$ eV); b – theoretical [ADC(3)/6-311G*]: $1 - 1a_2(\pi_3)$; $2 - 2b_1(\pi_2)$; $3 - 6a_1$; $4 - 1b_1(\pi_1)$; $5 - 4b_2$, $6 - 5a_1$, $7 - 3b_2$; $8 - 4a_1$, $9 - 2b_2$, $10 - 3a_1$, $11 - 2a_1$, $12 - 1b_2$, $13 - 1a_1$.

Assignment of photoelectron spectra. The results of the calculations reproduce to a good qualitative level the main features of the experimental spectra in all cases, including the portion of the spectral envelope pertaining to the complex region of the inner-valence ionization. Assignment of the photoelectron spectra of furan, pyrrole, thiophene, and selenophene, according to the results obtained by us, do not therefore present particular difficulties.

As is well shown in Figs. 1-4 the ionization spectra of the calculated molecules have much in common, which is evidently reflected by the similarity in their behavior and electronic structure. Five basic region visuall well different from each other can be isolated in all the spectra.

The first region at $E<11eV$ includes in the furan and pyrrole spectra two peaks (A, B), which converge as one in the thiophene and selenophene spectra. These portions of the spectra are formed as a result of $1a_2(\pi_3)^{-1}$ and $2b_1(\pi_2)^{-1}$ transitions, the first of which, according to our data, is on the whole energetically preferable to the second. Only for selenole did the calculations predict the reverse order of transitions. However, in view of the very small difference between the calculated ionization energies (~0.04 eV) it is not possible to establish this unequivocally.
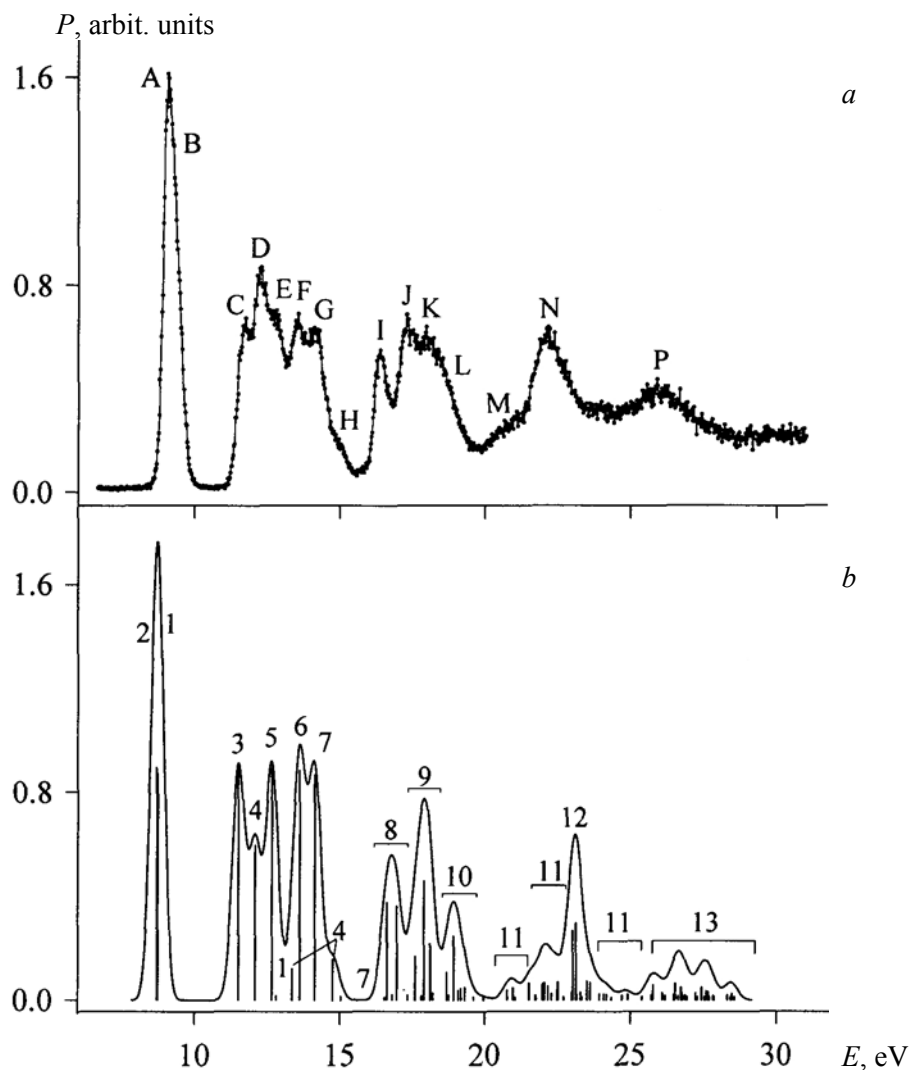

Fig. 4. Photoelectron spectra of selenole: a – experimental [29] ($h\nu = 80$ eV); b – theoretical [ADC(3)/6-311G*]: $1 - 1a_2(\pi_3)$; $2 - 2b_1(\pi_2)$; $3 - 6a_1$; $4 - 1b_1(\pi_1)$; $5 - 4b_2$, $6 - 5a_1$, $7 - 3b_2$; $8 - 4a_1$, $9 - 2b_2$, $10 - 3a_1$, $11 - 2a_1$, $12 - 1b_2$, $13 - 1a_1$.

The second region corresponds to the range 11-15 eV with a fairly complex system of bonds, in which up to five spectral maxima (C−G) may be separated. In these parts of the spectrum the contribution of transitions $6a_1^{-1}$, $1b_1(\pi_1)^{-1}$, $4b_2^{-1}$, $5a_1^{-1}$, and $5b_2^{-1}$ are introduced, the sequence of which in each actual case determines the final shape of the spectral envelope and the number of maxima in it.

A small number of satellites are present in this region together with the main lines. These satellites are mainly connected with a $1b_1(\pi_1)^{-1}$ transition, the line of which is absent "in a pure form", since it is broken into several weaker components. Each of these transitions is connected with final states in which the configuration $1b_1(\pi_1)^{-1}$ is displaced with various configurations of the $2p$-$1h$ type (where both vacancies are in the outer occupied MO π_2 or π_3). Since such an intense formation of satellites is not observed for other transitions found in the region being considered, it may be said that for the MO $1b_1(\pi_1)$ the orbital picture of ionization is disturbed "selectively".

The third spectral region (16-20 eV) is significantly more diffuse in comparison with the previous and contains up to four maxima (I−L). The spectral bands in this region have a significantly more complex structure, caused by processes of ionization of MO $4a_1$, $3b_2$, and $3a_1$. Each band includes several compactly disposed components apart from a large number of weak satellites, pertaining to the mentioned MO.

The fourth and fifth regions of the spectra (20-23.5 and 23.5-26 eV respectively) are characterized by an even more diffuse structure. In these regions a mode of ionization predominates with complete emergence from the framework of the usual orbital picture, in which multielectron effects begin to play the main role. The transitions of $2p$-$1h$ type occurring here are intense, predominently due to interactions with configurations having vacancies in the $2a_1$ and $2b_2$ MO (structures M−O), and also $1a_1$ (structures P, Q). In this way the spectral intensity is distributed between a large number of weak satellite lines, the total effect of which leads to a change of shape of the spectral envelope.

It is possible to pick out the 15-16 eV region separately in the considered spectra, where for thiophene and pyrrole a weak, but well noticeable, maximum is observed, and for selenophene there is a shoulder on the spectral envelope (H). As is well evident from the results of the calculations the structure being discussed is caused by a strong "shake-up" satellite linked with the main $1b_1(\pi_1)^{-1}$ transition. According to the results obtained by us the relatively high spectral intensity of these satellites ($P \sim 0.2$) is a consequence of a strong interaction between the $1b_1(\pi_1)^{-1}$ configuration and various configurations in which two vacancies are found in the outer occupied π-type MO.

Disturbance of the Orbital Picture of Ionization for π_1-MO. It has already been recorded above that the $2h$-$1p$ satellites observed in the outer valence region may be classified as "shake-up" satellites [33], linked with π_3- and π_1-MO. The effects of shifting the intensity from a $1h$ to a $2h$-$1p$ transition are most powerful in the case of the deeply-lying $\pi_1(1b_1)$-MO. This leads, in particular, to a reduction in the intensity of the main transition line $1b_1(\pi_1)^{-1}$. A similar effect, touching upon the inner π-MO, was detected previously in the theoretical study of photoelectron spectra of aromatic systems [41].

As analysis shows for π_1-MO the one-electron mode of ionization is disturbed due to its specific spatial properties, which are close to the properties of the unoccupied $\pi_4{}^*$-MO corresponding to it. The similar spatial characteristics of these MO assist a strong interaction of configurations $(\pi_1)^{-1}$ and $(\pi_i)^{-1}(\pi_i)^{-1}(\pi_4{}^*)$, where $i = 2, 3$. The strength of such an interaction is described approximately by the two-electron integral $(\pi_1\pi_4{}^*|\pi_i\pi_i)$, which may assume fairly large values, since the π_1- and $\pi_4{}^*$- orbitals occupy one and the same region of space.

An analogous happening occurs in the case of the π_3- and $\pi_5{}^*$-MO, but the formation of satellites is here not so marked. The π_2-MO is linked at its origin with the unshared pair (UP) of the heteroatom and has no corresponding vacant π-MO. By reason of its unbonding character, to a significant degree, the π_2-MO only overlaps the vacant MO of other types to a small extent. The $(\pi_2)^{-1}$-configuration may not therefore effectively interact with $2h$-$1p$ configurations which are appropriate in energy and the absence of satellites linked with the π_2-MO from the spectra is explained.

Aspects of the Ionization of the $2a_2(\pi_3)$- and $4b_1(\pi_2)$-Orbitals. One of the differences between the spectra of the molecules being discussed is the reduction in energy difference between the $2a_2(\pi_3)^{-1}$ and $4b_1(\pi_2)^{-1}$ states in the series furan, pyrrole, thiophene, and selenophene, which is caused by the approach in energy of the π_2-MO to the π_3-MO. Such behavior is readily explained by the properties of these MO. The π_3-MO energy is in all cases practically unchanged (with the exception of pyrrole, where the appearance of an additional hydrogen atom shows up), since this MO describes the butadiene fragment common to all the molecules. The reduction in ionization energy of π_2-MO occurs because of its relationship with the UP of the heteroatom, the potential for ionization of which is reduced in the series O, N, S, Se.

According to the results of the ADC(3) method the gap between the $^2A_2(\pi_3^{-1})$ and $^2B_1(\pi_2^{-1})$ states is 1.48, 0.74, 0.30, and 0.04 eV for furan, pyrrole, thiophene, and selenophene respectively. On drawing these states together their vibrational interaction becomes probable due to the oscillating modes of the b_2 symmetry. The presence of such interaction and the strength of nonadiabatic effects in the series furan-pyrrole-thiophene is confirmed by our work [53]. It is evident that even stronger nonadiabatic effects must be expected in the case of selenole, where according to the data obtained the energy interval between $^2A_2(\pi_3^{-1})$ and $^2B_1(\pi_2^{-1})$ is the minimum.

On the basis of the results of quantum-chemical calculations by the one-particle Green's function method, using the third order approximation of the algebraic diagram construction, the ionization spectra of the outer and inner valence ranges of key five-membered heteroaromatic molecules, furan, pyrrole, thiophene, and selenole have been analyzed for the first time. The calculated energies and intensities of vertical transitions are in good agreement with the newest experimental data and enable reliable assignment and interpretration of the observed photoelectron structures up to 30 eV to be carried out. It was shown that the effects of electron correlation begin to play a significant role in the upper portion of the inner valence range, which, in particular, is caused by the development of low-lying photoelectron satellites, linked with the inner π_1-orbitals. A set of rules and tendencies for the behavior of photoelectron spectra has been developed, which must to a significant extent be common for the whole class of heteroaromatic systems and their derivatives.

REFERENCES

1. A. R. Katritzky and A. F. Pozharskii, *Handbook of Heterocyclic Chemistry*, Acad. Press, Amsterdam (2000).
2. A. Gossauer, *Die Chemie der Pyrrole*, Springer, Berlin (1974).
3. R. A. Jones, E. C. Taylor, and A. Weissberger (editors), *The Chemistry of Heterocyclic Compounds, Pyrroles*, Vol. 48, Pt. 1, Wiley, New York (1992).
4. R. A. Jones, E. C. Taylor, and A. Weissberger (editors), *The Chemistry of Heterocyclic Compounds, Pyrroles*, Vol. 48, Pt. 2, Wiley, New York (1992).
5. S. Gronowitz, E. C. Taylor, and A. Weissberger (editors), *The Chemistry of Heterocyclic Compounds, Thiophene and Its Derivatives*, Vol. 44, Wiley, New York (1991) Pt. 4.
6. J.-L. Bredas and R. Silbey (editors), *Conjugated Polymers: The Novel Science and Technology of Highly Conducting and Nonlinear Optically Active Materials*, Kluwer, Dordrecht (1991).
7. E. Weigold and I. McCarthy, *Electron Momentum Spectroscopy*, Kluwer, New York (1999).
8. K. Kimura, S. Katsumata, Y. Achiba, T. Yamazaki, and S. Iwata, *Handbook of He I Photoelectron Spectra of Fundamental Organic Molecules*, Halsted, New York (1981).
9. D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, *Molecular Photoelectron Spectroscopy*, Wiley, London (1970).
10. M. H. Palmer, I. C. Walker, C. C. Ballard, and M. F. Guest, *Chem. Phys.*, **192**, 111 (1995).

11. E. E. Rennie, C. A. F. Johnson, J. E. Parker, D. M. P. Holland, D. A. Shaw, M. A. MacDonald, M. A. Hayes, and L. G. Shpinkova, *Chem. Phys.*, **236**, 365 (1998).
12. M. H. Palmer, I. C. Walker, and M. F. Guest, *Chem. Phys.*, **238,** 179 (1998).
13. E. E. Rennie, C. A. F. Johnson, J. E. Parker, R. Ferguson, D. M. P. Holland, and D. A. Shaw, *Chem. Phys.*, **250**, 217 (1999).
14. M. H. Palmer, I. C. Walker, and M. F. Guest, *Chem. Phys.*, **241**, 275 (1999).
15. P. J. Derrick, L. Asbrink, O. Edqvist, and E. Lindholm, *Spectrochim. Acta*, **27A**, 2525 (1971).
16. P. J. Derrick, L. Asbrink, O. Edqvist, B.-O. Jonsson, and E. Lindholm, *Int. J. Mass Spectrom. Ion Phys.*, **6**, 161 (1971).
17. P. J. Derrick, L. Asbrink, O. Edqvist, B.-O. Jonsson, and E. Lindholm, *Int. J. Mass Spectrom. Ion Phys.*, **6**, 177 (1971).
18. P. J. Derrick, L. Asbrink, O. Edqvist, B.-O. Jonsson, and E. Lindholm, *Int. J. Mass Spectrom. Ion Phys.*, **6**, 191 (1971).
19. G. Bieri, L. Asbrink, and W. von Niessen, *J. Electron Spectrosc. Relat. Phenom.*, **27**, 129 (1982).
20. J. A. Sell and A. Kuppermann, *Chem. Phys. Lett.*, **61**, 355 (1979).
21. M. Takahasi, K. Otsuka, and Y. Udagawa, *Chem. Phys.*, **227**, 375 (1998).
22. M. Takahasi, R. Ogino, and Y. Udagawa, *Chem. Phys. Lett.*, **288**, 821 (1998).
23. U. Gelius, C. J. Allan, G. Johansson, H. Siegbahn, D. A. Allison, and K. Siegbahn, *Phys. Scr.*, **3**, 237 (1971).
24. A. D. O. Bawagan, B. J. Olsson, K. H. Tan, J. M. Chen, and B. X. Yang, *Chem. Phys.*, **164**, 283 (1992).
25. T. Munakata, K. Kuchitsu, and Y. Harada, *J. Electron Spectrosc. Relat. Phenom.*, **20**, 235 (1980).
26. N. Kishimoto, H. Yamakado, and K. Ohno, *J. Phys. Chem.*, **100**, 8204 (1996).
27. S. F. Zhang, X. G. Ren, G. L. Su, C. G. Ning, H. Zhou, B. Li, G. O. Li, and J. K. Deng, *Chem. Phys.*, **327**, 269 (2006).
28. D. M. P. Holland, L. Karlsson, and W. von Niessen, *J. Electron Spectrosc. Relat. Phenom.*, **113**, 221 (2001).
29. I. Powis, I. L. Zaytseva, A. B. Trofimov, J. Schirmer, D. M. P. Holland, A. W. Potts, and L. Karlsson, *J. Phys. B: At. Mol. Opt. Phys.*, **40**, 2019 (2007).
30. A. B. Trofimov, J. Schirmer, D. M. P. Holland, L. Karlsson, R. Maripuu, K. Siegbahn, and A. W. Potts, *Chem. Phys.*, **263**, 167 (2001).
31. A. W. Potts, A. B. Trofimov, J. Schirmer, D. M. P. Holland, and L. Karlsson, *Chem. Phys.*, **271**, 337 (2001).
32. A. B. Trofimov, J. Schirmer, D. M. P. Holland, A. W. Potts, L. Karlsson, R. Maripuu, and K. Siegbahn, *J. Phys. B: At. Mol. Opt. Phys.*, **35**, 5051 (2002).
33. L. S. Cederbaum, W. Domcke, J. Schirmer, and W. von Niessen, *Adv. Chem. Phys.*, **65**, 115 (1986).
34. W. von Niessen, L. S. Cederbaum, and G. H. F. Diercksen, *J. Am. Chem. Soc.*, **98**, 2066 (1976).
35. W. von Niessen, W. P. Kraemaer, and L. S. Cederbaum, *J. Electron Spectrosc. Relat. Phenom.*, **8**, 179 (1976).
36. G. De Alti and P. Decleva, *Chem. Phys. Lett.*, **77**, 413 (1981).
37. M. Ehara, Y. Ohtsuka, H. Nakatsuji, M. Takahashi, and Y. Udagawa, *J. Chem. Phys.*, **122**, 234319-01 (2005).
38. W. von Niessen, J. Schirmer, and L. S. Cederbaum, *Comp. Phys. Rep.*, **1**, 57 (1984).
39. J. Schirmer, L. S. Cederbaum, and O. Walter, *Phys. Rev. A.*, **28**, 1237 (1983).
40. J. Schirmer and G. Angonoa, *J. Chem. Phys.*, **91**, 1754 (1989).
41. M. S. Deleuze, A. B. Trofimov, and L. S. Cederbaum, *J. Chem. Phys.*, **115**, 5859 (2001).
42. A. W. Potts, D. M. P. Holland, A. B. Trofimov, J. Schirmer, L. Karlsson, and K. Siegbahn, *J. Phys. B: At. Mol. Opt. Phys.*, **36**, 3129 (2003).

43.   A. B. Trofimov, J. Schirmer, V. B. Kobychev, A. W. Potts, D. M. P. Holland, and L. Karlsson, *J. Phys. B: At. Mol. Opt. Phys.*, **39**, 305 (2006).

44.   W. J. Hehre, R. Ditchfield, and J. A. Pople, *J. Chem. Phys.*, **56**, 2257 (1972).

45.   R. Krishnan, J. S. Binkley, R. Seeger, and J. A. Pople, *J. Chem. Phys.*, **72**, 650 (1980).

46.   T. Clarck, J. Chandrasekhar, G. W. Spitznagel, and P. v. R. Schleyer, *J. Comput. Chem.*, **4**, 294 (1983).

47.   P. C. Hariharan and J. A. Pople, *Theoret. Chimica Acta*, **28**, 213 (1973).

48.   A. D. McLean and G. S. Chandler, *J. Chem. Phys.*, **72**, 5639 (1980).

49.   L. A. Curtiss, M. P. McGrath, J.-P. Blandeau, N. E. Davis, R. C. Binning, Jr., and L. Radom, *J. Chem. Phys.*, **103**, 6104 (1995).

50.   O. Walter and J. Schirmer, *One-Particle Green's Function ADC(3) Code*; G. Angonoa and J. Schirmer, *The Constant Diagram Code*, Further Developed by M. K. Scheller and A. B. Trofimov, TC/PCI/ Heidelberg University, 1984-2002.

51.   M. W. Schmidt, K. K. Baldridge, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. J. Su, T. L. Windus, M. Dupuis, and J. A. Montgomery, *J. Comput. Chem.*, **14**, 1347 (1993).

52.   M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, and J. A. Pople, *Gaussian 98, Revision A.7*, Gaussian Inc., Pittsburgh PA (1998).

53.   A. B. Trofimov, H. Kőppel, and J. Schirmer, *J. Chem. Phys.*, **109**, 1025 (1998).