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Photoelectron spectra of molecules. Part 12. Vinyl, allyl, and phenyl ethers and sulphides

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Abstract

He I (21.21 eV) photoelectron spectra of 21 vinyl, allyl, and phenyl ethers and sulphides are measured: $\text{H}_2\text{C}=\text{CHOC}_3\text{H}_7$, $\text{H}_2\text{C}=\text{CHOC}_6\text{H}_5$, $\text{Cl}_2\text{C}=\text{CHOCH}_3$, $\text{Cl}_2\text{C}=\text{CHOC}_2\text{H}_5$, $\text{Cl}_2\text{C}=\text{CHOCH}_2\text{CH}_2\text{Cl}$, $\text{H}_2\text{C}=\text{CHCH}_2\text{OC}_2\text{H}_5$, $\text{H}_2\text{C}=\text{CHCH}_2\text{OC}_6\text{H}_5$, $(\text{H}_2\text{C}=\text{CHCH}_2)_2\text{O}$, and $\text{H}_2\text{C}=\text{CHSC}_3\text{H}_7$, $\text{H}_2\text{C}=\text{CHSC}_6\text{H}_5$, $\text{H}_2\text{C}=\text{CHSC}(\text{CH}_3)_3$, $(\text{H}_2\text{C}=\text{CH})_2\text{S}$, $\text{H}_2\text{C}=\text{CHCH}_2\text{SC}_2\text{H}_5$, $\text{H}_2\text{C}=\text{CHCH}_2\text{SC}_6\text{H}_5$, $(\text{H}_2\text{C}=\text{CHCH}_2)_2\text{S}$, $\text{H}_2\text{C}=\text{CHSC}_2\text{H}_5$, $(\text{ClCH}_2\text{CH}_2)_2\text{S}$, $\text{C}_6\text{H}_5\text{OCH}_3$, $\text{C}_6\text{H}_5\text{OC}_2\text{H}_5$, $\text{C}_6\text{H}_5\text{SCH}_3$, $\text{C}_6\text{H}_5\text{SC}_2\text{H}_5$. The main goal of this treatment was to compare the structural effects in two closely related classes of compounds: oxygen-containing vinyl compounds and analogous ones containing sulfur. To clarify the various aspects of the substituent effects on the behavior of ionization centers in the gas phase, some chlorosubstituted compounds are included. The photoelectron spectra have been recorded and analyzed on the basis of correlation with the spectra of related compounds for which assignments are established. Ab initio quantum chemical calculations with a complete optimization of the geometry were accomplished for interpretation of the spectra as well. The Gaussian-98 system of programs was applied using 6-31G* basis set. For comparison, the density functional theory (DFT) using the B3LYP hybri   functional and a 6-31G* basis set was also employed.    2002 Elsevier Science B.V. All rights reserved.

Keywords: ethers; sulphides; photoelectron spectra

1. Introduction

In a series of articles, a systematic study of electronic structure, geometry and their correlation to chemical properties for different classes of compounds is developed using photoelectron spectra. In a previous publication, the analysis of photoelectron spectra of organic acids and their ethers was reported [1]. Throughout the complex approach and quantum chemical calculations for interpretation of photoelectron spectra developed in Ref. [2] were employed. In

this communication we present the photoelectron spectra of some vinyl, allyl and phenyl ethers and sulphides. The assignment of main bands in spectra is obtained from ab initio and DFT calculations [3] and from comparison with the well-established spectra.

PES represents an appropriate means of obtaining information about orbital energies of occupied MOs and interactions between particular molecular skeletons and the substituents. The interesting properties of vinyl ethers and sulphides arise from the direct linkage of an atom with lone-pair electrons and the C=C bond, which, under favorable spatial orientation leads to the effective $n-\pi$ conjugation. These compounds

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provide an excellent test for the studies of $n-\pi$ -interactions. If we assume that the experimental bands can be connected to the definite orbitals, changes in the location, order, and shape of the bands with the molecular structure are accounted for by the intramolecular orbital–orbital interaction and by the changes in the charge distributions. The contribution of the conjugation depends also on the nature, number, and position of substituents attached to this system. The interaction of double-bond π -electrons and nonbonding electron pairs on oxygen or sulfur atom influence upon the electronic and spatial structure of allyl and vinyl ethers and sulphides substantially. PES is used for conformation analysis of compounds with adjacent lone pairs or π -systems provided that the ionization bands under consideration are unambiguously assigned and inductive effect and secondary orbital interactions are negligible or eliminated [4].

The structures and thermodynamic stability of vinyl ethers have been studied extensively by several techniques [5–11] including chemical equilibration [12], dipole moment measurements [13] and ^{13}C nmr spectroscopy [14]. In Ref. [5], the ^{17}O nmr chemical shifts of alkyl-substituted vinyl ethers recorded in CDCl_3 solution are reported, and the relationship between structure and chemical shift is explored.

The PE spectrum of methyl vinyl sulphide has been recorded over the range of temperature 20–600°C. The observed spectra changes are quantitatively explained in terms of a temperature dependent equilibrium between *cis* and *gauche* rotamers of this molecule [15]. The energy difference between both is measured to be 2.3 ± 0.2 kcal/mol with the *cis* form ($\vartheta = 0^\circ$), being the more stable one. The result was supported by RHF-SCF/6-31G* calculations. Electron diffraction experiment [16] exhibits this compound to be in gas phase 2:1 mixture of *cis* conformation C_s and C_1 with torsion angle 106° .

PE study of vinyl alcohol has been reported [17,18]. The first band is due to the excitation of an electron from the π -MO which is essentially antibonding between the oxygen atom and the vinyl group. The region of the first band shows evidence of a weaker, second component which is expected to be a less abundant conformer. Ab initio SCF-MO calculations were carried out for vinyl alcohol at the experimentally determined geometry using a 4-31G basis set [19,20]. The region of the first band shows

evidence of an underlying, weaker, second component [17]. It was expected that two rotameric forms (*cis*- and *trans*-vinyl alcohol) are present with less abundant anti-conformer. PES of vinyl halides and of methyl vinyl ether has been measured [21] and the second band was assigned to the lone pair orbital n_{O} .

In Ref. [22], the PES for the π -donor-substituted allenes $\text{RCH}=\text{C}=\text{CH}_2$, such as $\text{R}=\text{OCH}_3$, OC_2H_5 , $\text{OC}(\text{CH}_3)_3$, SCH_3 , SC_2H_5 , $\text{SC}(\text{CH}_3)_3$ are reported and assignments of PE bands are presented. Interactions of the substituents with the remote allenic $\text{C}=\text{C}$ moiety are rationalized through Coulombic field effects and hyperconjugation. The lowest energy ionic states have geometry which deviates considerably from those of the neutral ground state. Furthermore, it is shown that all the radical cations exist in one largely preferred conformation. For the methyl and ethyl compounds it is the *cis* conformation, whereas for $\text{OC}(\text{CH}_3)_3$ and $\text{SC}(\text{CH}_3)_3$ the *trans* form is preferred [23].

In Ref. [24], the UV and PE spectra of methyl vinyl ether and ethyl vinyl thioether are compared. The significant similarity between the PES of related ethers and thioethers is stressed. In the case of saturated thioethers the corresponding uv spectra are, however, very different, showing that the involvement of sulfur 3d orbitals is important in the low excited states of saturated sulfur compounds. There is no evidence for the participation of sulfur 3d AOs in the low-lying excited states of unsaturated thioethers.

The density functional theory (DFT) would seem natural to consider since it, in this context, accounts for dynamical correlation and possesses good particle scaling. However, its use has been hampered by the lack of a direct interpretation of the orbital energies corresponding to Koopmans' theorem in Hartree–Fock theory. However, the eigenvalue of the Kohn–Sham [25] (KS) orbitals equals the negative of the ionization energy only if the essentially exact exchange–correlation potential is used [26]. So, the actual quality of KS eigenvalues for estimating ionization energies is depending on the choice of approximate functional. The B3LYP functional utilized in this work is not truly a KS–DFT method. It mixes KS–DFT and HF. Therefore, neither Koopmans' theorem, nor Janak theorem apply there.

In the recent years the chemists have begun to apply KS orbitals in rationalizing chemical phenomena, as it is done with MO-s. The early attempts to compare the

results of quantum chemical calculations with the experimental data refer to the energies of the occupied MO-s. According to the Koopmans' theorem for the closed shell molecule the ab initio SCF energy of MO is approximately equal to the negative of the energy of ionization of the electron from this orbital. At the same time the invariability of the MO (the lack of the reorganization of the electron shell) and the constancy of the electron correlation energy contribution into the total energy is assumed during the transfer of the molecule to the ion-radical state during the ionization process.

The failure to take into account the stabilization of the ion-radical due to the reorganization of the MO during the ionization process leads to the overestimated values of ionization energies. At the same time negligence to account for the non-zero difference in the correlation energies of the cation-radical and the molecular ground state (the latter, most likely has larger correlation energy than the former) is responsible for the underestimated values of ionization energies. Hence, only when the sum of these two contributions is constant or depends lineary on the ionization energy one should expect the observance of the linear relationship between ionization potential (IP) and MO energy $IP = a\epsilon_{SCF} + b$, where a and b are constants. Only in the limiting special case of the total exact compensation of these contributions, or in the case of invariability of their difference in the process of ionization this equation reduces to the simple proportionality. In this connection, it is necessary to mention that the increase of the extent of the localization of the corresponding MO leads to the increase of the expected contribution from the energy of reorganization. The reason why HF tends to work is because HF approximation ignores correlation effects and Koopmans' theorem ignores electronic relaxation of the created cation and the effects are of the opposite sign.

Also, sometimes there are additional limitations to the Koopmans' theorem for the open shell molecules, which are due to the partial inability of the simple Slater determinant to represent adequately the wavefunctions of such a species.

The DFT accounts for exchange correlation. However, by assuming KS orbital energies equal to the negative of ionization energies one ignores the electronic relaxation of the newly created cation. As

the correlation energy stabilizes preferably the ground state, it results in too high IP calculated values. Moreover, DFT frequently orders orbitals differently than HF.

Apparently though, some interpretation of the KS orbital energies is possible. The shape and symmetry properties of the KS orbitals are very similar to those calculated by HF method and the energy order of the occupied orbitals is in most cases in agreement among the various methods. It was established [27] that an approximately linear dependence of $(\epsilon_i^{KS} - \epsilon_i^{HF})$ on $\epsilon_i^{HF} \sim IP$ for the occupied as well as for the unoccupied orbital eigenvalues holds. In other words, KS energies differ from the HF MO energies, but they tend to be linearly related, at least for calculations utilizing commonly used functional. At the present time, a number of developments in DFT have led to significant improvement in the ability to calculate gas-phase ionization energies, so that detailed comparison with experimental data has become meaningful.

Applications of DFT techniques for valence ionization potentials have become available [28–32]. The typical energy difference between IP_i and $-\epsilon_i^{B3LYP}$ values are about 2 eV for stilbene, styrylthiophenes, and pyridines [33].

In Ref. [34], the authors have done a systematic study of small molecules using various DFT methods and the G2 thermochemical data set. They found that the B3LYP functional gave mean absolute deviations of 0.15 eV for basis set of spdf quality. Fox and Kollman [35] in their study of substituted benzenes agree that the B3LYP functional is the best suited to IP studies, usually being superior to ab initio methods such as MP2 that often show serious spin contamination in the cation.

The ionization potentials of 55 para- and 55 meta-disubstituted benzenes, consisting of binary combinations of electron-withdrawing and electron-donating groups have been calculated [36] using DFT with the B3LYP functional and a 6-31G* basis set. Relative ionization potentials, referred to benzene, are compared with experimental values and shown to be in good agreement. Calculations on mono- and poly-substituted benzenes [37] by obtaining geometries and frequencies at the AM1 level, followed by B3LYP single-point energy calculation are performed. One could obtain IP-s for monosubstituted benzenes that differed systematically from experiment by ca.

10 kcal/mol (0.43 eV) for a 6-31G* basis set, or 5 kcal/mol (0.22 eV) for a 6-311G* basis set. However, no improvement in correlation coefficient was noted while going to the larger basis set, and thus, these systematic errors could easily be corrected for by simply referring IP values to a suitable reference obtained calculated with the same basis set. When that was done they obtained $\Delta\text{IP} = \text{IP}(\text{benzene reference}) - \text{IP}(\text{substituted benzene})$, and these ΔIP values will be shown to correlate very well with experimental data, also taken as ΔIP -s. In Ref. [38], DFT calculations of substituted ethenes were performed.

The KS orbital formulation of DFT together with transition potential techniques (variation principle is applied to densities referring to a state with a fractional occupancy) was used [39,40] for the direct calculation of IP-s and chemical shifts in the core region with high accuracy. The original study was followed by several works [32,41–48] for spectra. The results of local density approximation (LDA) calculations [32] indicate that the correlation functional is capable of accurately including the valence correlation error, while the transition potential technique accounts for the relaxation.

The triplet and singlet excited states of methyl vinyl ether have been characterized [49] by electron loss spectroscopy and multireference DFT with configuration interaction (DFT/MRCI). The B3LYP exchange correlation functional was employed. The results are complemented by a study of ethyl vinyl ether, methyl allyl ether, and benzyl methyl ether. The *cis* structure considered is found to be more stable by 2.0 kcal/mol than the *trans* conformer.

The purpose of this work has been to contribute to the elucidation of problems such as the nature of the interaction of the oxygen/sulfur lone pairs with double bonds and to clear up some of the band assignments through the measurement of the PE spectra of some unsaturated sulfur compounds and their comparison with the parent oxygen compounds. The conclusions drawn are used to assign some MO-s in more complex oxygen and sulfur compounds with vinyl, allyl and phenyl substituents. On the other hand, the order of MO-s on the energy scale is dependent on the conformation of the molecule. *Ab initio* calculations with full optimization of geometry are employed to find out the favor geometry of such compounds in gas phase.

We would like to see if a ‘Koopman’s theorem-like’ association of IP-s with KS eigenvalues calculated with common functional might work. One expects that this work offers an additional test of a question whether the KS eigenvalues provide an energy ordering of the orbitals that resembles or differs from that given by HF SCF one-electron scheme. The experimental IP-s measured by PES in case of more complex organic molecules with different electronic structure provide an additional probe.

2. Experimental and calculations

The HeI photoelectron spectra of the seven vinyl ethers, four vinyl sulphides, three allyl ethers, three allyl sulphides and some related compounds together with combined substituents have been recorded. A photoelectron spectrometer equipped with a cylinder type analyzer was used to obtain the spectra. This instrument has been described previously [2]. Samples that were liquid at room temperature and atmospheric pressure were degassed prior obtaining spectra by alternate freezing in liquid nitrogen, evacuation of the sample vessel, and unthawing with the stopcock to the vacuum pump closed. All samples were degassed by several freeze–pump–thaw cycles before use. Calibration of the ionization energy scale was carried out by reference to peaks due to admixed inert gas Ar (Argon doublet at 15.759 and 15.937 eV). The PE spectra reported in the present work are the averaged representations of the results of several measurements. The vertical IP-s are determined as the location of the maximum of the corresponding peak. On the other hand, ionization potentials in PES should be considered adiabatic only in the case when the analysis of the vibrational structure of the given band identifies this ionization process as a 0–0 transfer. However, our experience shows that the IP-s determined at the beginning of the slope of the spectral band, which is shifted on the energetic scale by the half width of the argon line, coincide with the adiabatic values determined by the photoionization technique within ± 0.03 eV. The vacuum monochromator [50] (the resolution of ≤ 0.03 eV) Seya–Namioka was used for the determination of first adiabatic IP-s from photoionization procedure.

Part of the reagents used throughout of the present

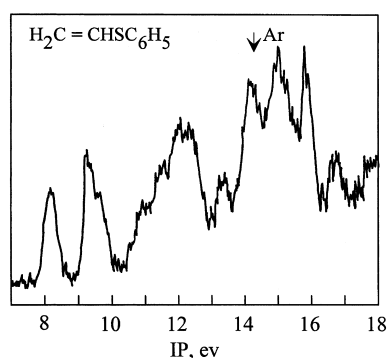
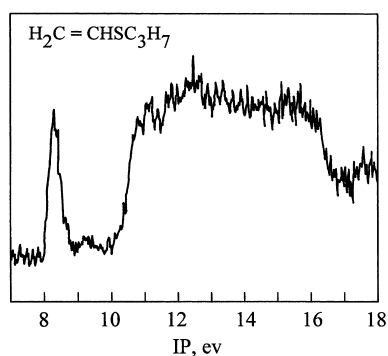
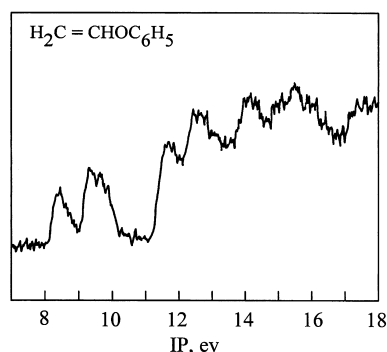
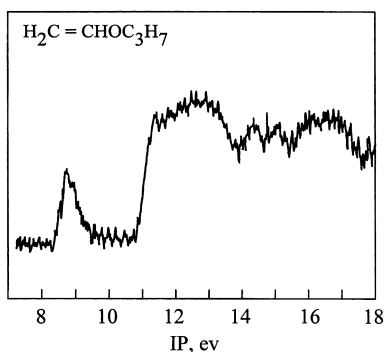


Fig. 1. Experimental photoelectron spectra of $\text{H}_2\text{C}=\text{CHOC}_3\text{H}_7$ and $\text{H}_2\text{C}=\text{CHSC}_3\text{H}_7$.

Fig. 2. Experimental photoelectron spectra of $\text{H}_2\text{C}=\text{CHOC}_6\text{H}_5$ and $\text{H}_2\text{C}=\text{CHSC}_6\text{H}_5$.

series of paper is commercially available. Some of the compounds were kindly delivered by Professor V.A.Trofimov and are synthesized [51] at Irkutsk Institute of Organic Chemistry, Irkutsk, Russia. The purity was controlled by g.l.c.

Figs. 1–10 show the PES recorded in this work. Values of adiabatic and vertical IP-s determined are represented in Table 1 together with some literature data and calculated values for comparison. To assign the PE spectral bands and estimate the geometry of molecules the RHF calculations were applied using 6-31G* basis set. In density functional (DFT) calculations the three-parameter hybrid nonlocal exchange correlation functional proposed by Becke [52,53] has been employed. Nonlocal correlation is approximated by the Lee–Yang–Parr functional [54] (B3LYP), the 6-31G* basis set was used. Calculations were performed using the Gaussian 98 program package [55]. Standard symbols have been used in order to denote the MO symmetry and the approximate nature of its localization. The relevant data are available in

Table 1. As a rule, in treated compounds the HOMO is essentially localized at the $\text{C}=\text{C}-\text{O}(\text{S})$ subunit and has a node between the vinylic and the alkoxy moieties. The n_{O} or n_{S} corresponds to the lone pair (perpendicular to the vinyl plane) of oxygen or sulfur, respectively (Table 1). In Table 2 are given the main features of geometry calculations.

3. Results and discussion

The interpretation of PE spectra of organic compounds usually relies on Koopmans' theorem. Here, the experimental vertical ionization energy is related to the negative ground state orbital energy calculated with a SCF procedure. Koopmans' breakdown may be due to non-adiabatic effects, but also vibrational effects, which can be understood in the context of the adiabatic approximation and the Franck–Condon principle may complicate interpretation of PE spectra [22]. For radical cations the extent

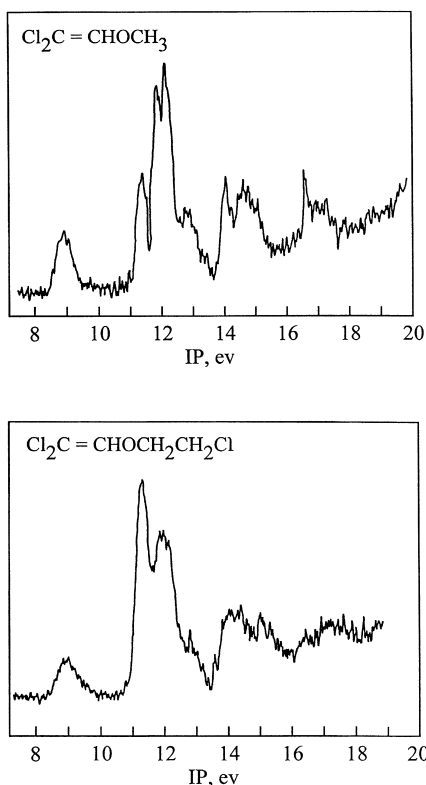


Fig. 3. Experimental photoelectron spectra of $\text{Cl}_2\text{C}=\text{CHOCH}_3$ and $\text{Cl}_2\text{C}=\text{CHOCH}_2\text{CH}_2\text{Cl}$.

of vibronic coupling between two electronic states becomes smaller with increasing delocalization of the orbitals across the molecular skeleton and the substituents [56–58]. As noted in Ref. [22] the OAlk groups are relatively strong π -donors and SAlk groups are weaker π -donors with large deloca-

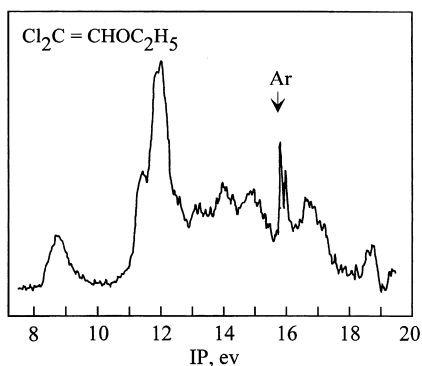


Fig. 4. Experimental photoelectron spectrum of $\text{Cl}_2\text{C}=\text{CHOC}_2\text{H}_5$.

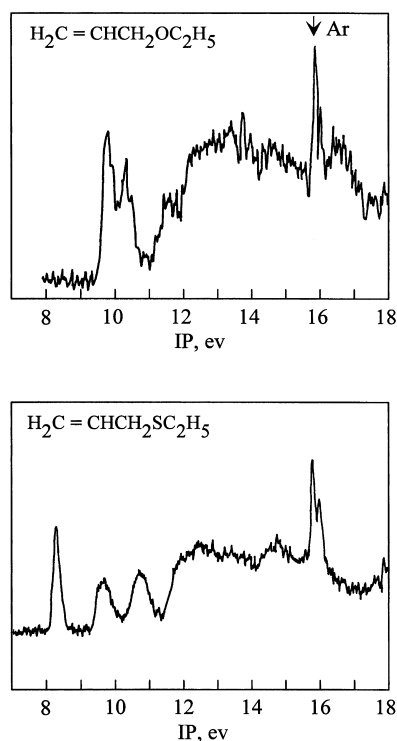


Fig. 5. Experimental photoelectron spectra of $\text{H}_2\text{C}=\text{CHCH}_2\text{OC}_2\text{H}_5$ and $\text{H}_2\text{C}=\text{CHCH}_2\text{SC}_2\text{H}_5$.

lization effects. Therefore, one can anticipate that in the PE spectra of vinyl compounds with these substituents vibronic effects will play a small or negligible role.

The types of interactions that have been observed in vinyl ethers and sulphides are resonance effect and the inductive effect of OR and SR groups. A resonance effect occurs as a result of interaction between $\pi(\text{C}=\text{C})$ orbital and the oxygen or sulfur nonbonding orbital which is perpendicular to the vinyl group plane (both orbitals are a'' in the C_s molecule). This combination produces two π orbitals, an antibonding combination predominantly of $\pi(\text{C}=\text{C})$ character and a bonding combination of predominantly non-bonding character. Acquisition of antibonding character in the $\pi(\text{C}=\text{C})$ orbital is confirmed by its destabilization and by the increase in the C–O or C–S stretching frequency of the ion relative to the neutral molecule. The first can be evaluated from ionization band vibrational structure. Evidence for acquisition of bonding character in the combination with

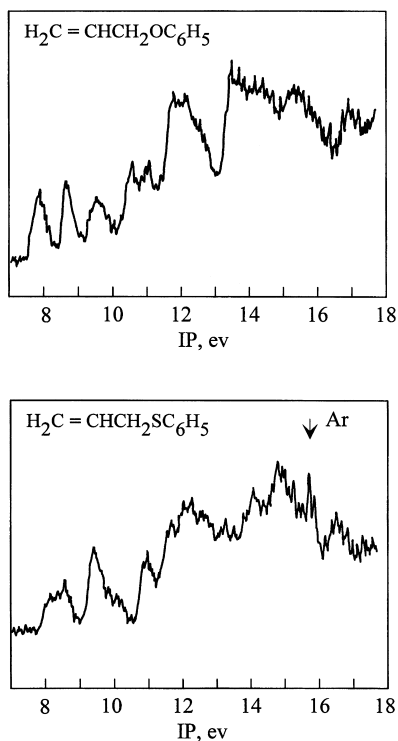


Fig. 6. Experimental photoelectron spectra of $\text{H}_2\text{C}=\text{CHCH}_2\text{OC}_6\text{H}_5$ and $\text{H}_2\text{C}=\text{CHCH}_2\text{SC}_6\text{H}_5$.

nonbonding character is its stabilization and the broadening of its relatively sharp nonbonding band in alkyl compounds. The inductive effect of the OR/SR group serves to draw electron density from the vinyl group to the substituent. In this case these are opposing simultaneous effects.

The first ionization energy (IE) band of methyl vinyl ether has vibrational fine structure so that an adiabatic value can be given 8.95 eV. The vertical IE is at 9.13 eV. The spacing [8,21] between the vibrational peaks is $1300 \pm 100 \text{ cm}^{-1}$. The PE spectra of ethyl and propyl vinyl ether reveal a regular decrease of ionization energy of both, first band indicated as π , and second assigned to the lone pair orbital n_{O} , due to the increasing inductive effect of alkyl groups. The HOMO is essentially localized at the $\text{C}=\text{C}-\text{O}$ subunit and has a node between the vinyl and alkoxy moieties. The change in electron population occurs mainly in the $\text{C}=\text{C}$ bond for all alkyl vinyl ethers making the mainly $\text{C}=\text{C}$ stretching frequency appear on the PE band (1300 cm^{-1}).

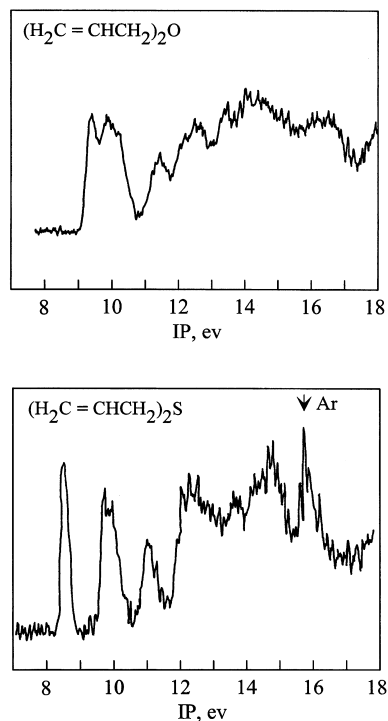


Fig. 7. Experimental photoelectron spectra of $(\text{H}_2\text{C}=\text{CHCH}_2)_2\text{O}$ and $(\text{H}_2\text{C}=\text{CHCH}_2)_2\text{S}$.

^{17}O NMR chemical shifts measured in solution are known to be sensitive to π electron density [59] the O atom, which is structure dependent. Characteristically, the ^{17}O atoms of alkyl vinyl ethers absorb several tens of ppm downfield from those of related saturated ethers [5], i.e. indicating less screening or less electron density on O. On the other hand, it causes growth of the $n-\pi$ conjugation. The reduced $\text{IE}(n_{\text{O}})$, pointing to increased electrondensity on the O atom, arise mainly from the electropositive nature of alkyl groups which opposes the separation of charge due to $n-\pi$ conjugation in the vinyloxy system. Therefore, methyl vinyl ether has the chemical shift [5] $\delta(^{17}\text{O}) = 57 \text{ ppm}$ (relative to water) and $\text{IE}(n_{\text{O}}) = 9.05 \text{ eV}$, whereas propyl vinyl ether has [5] 81 ppm and 8.86 eV (Table 1), respectively.

The effects of alkyl substituents attached to the vinyl moiety suggest a considerable decrease in $n-\pi$ conjugation in the vinyloxy system due to the electron-releasing inductive effect of the alkyl group, which tends to polarize the $\text{C}=\text{C}$ bond in a direction opposite to that caused by the alkoxy group [5]. Evidently, the

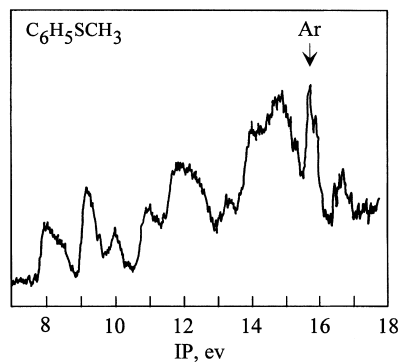
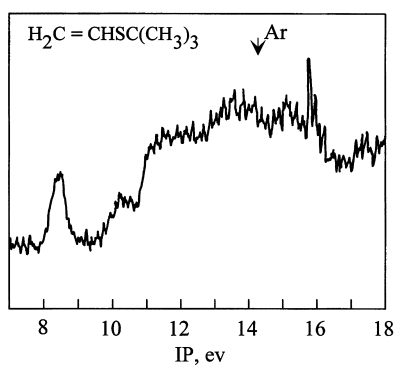
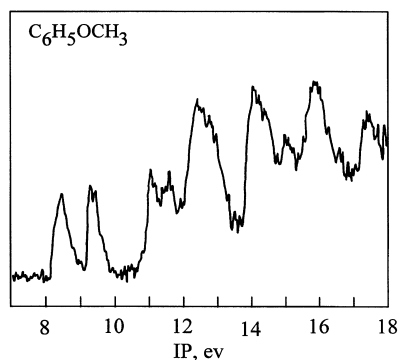
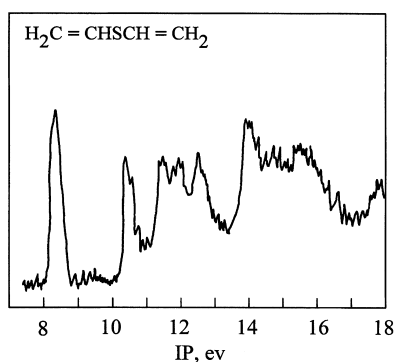


Fig. 8. Experimental photoelectron spectra of $(\text{H}_2\text{C}=\text{CH})_2\text{S}$ and $\text{H}_2\text{C}=\text{CHSC}(\text{CH}_3)_3$.

Fig. 9. Experimental photoelectron spectra of $\text{C}_6\text{H}_5\text{OCH}_3$ and $\text{C}_6\text{H}_5\text{SCH}_3$.

contribution of $n-\pi$ conjugation in alkyl vinyl ethers grows by the presence of chloro-substitution on the β -carbon. So, for $\text{Me}_2\text{C}=\text{CHOMe}$ the NMR shift is 28 ppm compared to 57 ppm for methyl vinyl ether [5]. On the other hand, the increase of n_{O} energy (from 12.05 to 12.54 eV) and decrease of π ionization energy (from 9.05 to 8.84 eV) in $\text{Cl}_2\text{C}=\text{CHOMe}$ compared to methyl vinyl ether, points to the effect mentioned above.

Methyl vinyl thioether has a PES very similar to that of methyl vinyl ether, except for a pronounced shift towards lower energies of most of the bands. Instead of a spacing of about 1300 cm^{-1} for the oxygen derivative one finds a spacing of 600 cm^{-1} . Also in the fine structure of this PE band the 0–0 transition is the most intense for the thioether while the maximum is at a higher member for the ether, indicating a lesser change of geometry upon ionization for the sulfur compound [24]. In the unsaturated ethers the frontier orbital is of π character, the O 2p or

S 3p lone pairs behaving as π atomic orbital. Hence, the vibration fine structure is dominated by the relatively high frequency C=C stretching vibration in ethers and the low frequency C–S vibration in thioethers. This is the probable explanation of the fact that the PE bands of the thioethers are much sharper than PE bands of the ethers. The first band in PES of divinyl thioether is quite narrow indeed. The same is true for diallyl sulphide (see Fig. 7). In the thioether the change is produced mainly around the sulfur atom and the vibration frequency which appears is mainly C–S stretching mode 600 cm^{-1} . Furthermore, the shapes of the PE band 1 of SCH_3 , SC_2H_5 , and SC_3H_7 are very similar and relatively sharp. Owing to the relatively small perturbation of the corresponding orbital when substituting methyl group by the other alkyl groups the band assignments for the alkyl vinyl ethers and sulphides in Table 1 are straightforward. In particular, π MO is continuously

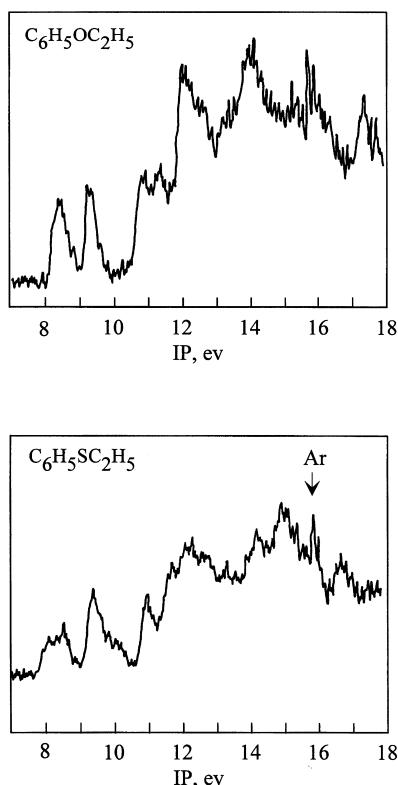


Fig. 10. Experimental photoelectron spectra of $\text{C}_6\text{H}_5\text{OC}_2\text{H}_5$ and $\text{C}_6\text{H}_5\text{SC}_2\text{H}_5$.

destabilized due to the substitution of CH_3 by C_2H_5 , C_3H_7 , and $\text{C}(\text{CH}_3)_3$.

For the vinyl ethers and vinyl sulphides several conformers may exist. Even within the limit of the validity of Koopmans' approximation the deduction of electronic effects of the substituent on the orbital energies of the considered compounds may be difficult due to the existence of conformer equilibrium. Discussion of conformer equilibria of such compounds generally refers to cis, trans, and gauche forms (dihedral angle 0° , 180° , and intermediate, respectively). Even within the limits of validity of Koopmans' approximation deduction of electronic effects of the substituents on the orbital energies of the considered compound may be difficult due to the existence of conformer equilibrium. For the compounds with single bonded groups such as OR and SR several conformers may exist. The lack of spatial symmetry in molecules with gauche conformations lifts the π – σ separation of MO-s. Then, it is no

longer possible to interpret substituent effects in terms of separated π and σ interactions.

The vibrational structures of first bands of $\text{R}=\text{CH}_3$, $\text{R}=\text{C}_2\text{H}_5$ and even $\text{R}=\text{CH}_2\text{CH}_2\text{Cl}$ in $\text{Cl}_2\text{C}=\text{COR}$ compounds are very similar indicating that the corresponding geometrical situations for these species are comparable. Furthermore, the shapes of the first PE band of CH_3 , C_2H_5 , and C_3H_7 substituted vinyl sulphides are very similar. They are relatively sharp, but asymmetric with the 0–0 transition probably being the most intense vibrational component. This means a lesser change of geometry upon ionization of the highest occupied MO of the sulfur compounds as compared to oxygen ones, which band is almost symmetric and the maximum at higher vibrational members. The situation is more complex for the $\text{H}_2\text{C}=\text{CHSC}(\text{CH}_3)_3$, whose first PES band is rather symmetric and broad and exhibits a vibrational structure different from those found for other alkyl substituted vinyl sulphides. Hence, the cation radical exhibits a geometry, which deviates considerably from that of neutral molecule and relative to methyl, ethyl, and propyl substitution the conformational situation has changed. One can expect the trans form to be the plausible one due to bulkiness of the tertial butyl group as it appears in tertiary alkylsubstituted allenes [23]. However, calculation at 6-31G* level results in the gauche ($\vartheta \approx 60^\circ$) form and DFT in the cis conformer as the most stable one for this compound. Our DFT calculations support the results of Ref. [15], the cis form as most stable for methyl vinyl sulphide (HF with 6-31G* prefers the trans form), where the C–S/ π hyperconjugation is not allowed but the n – π interaction is fully expressed. The effect is mainly due to the stabilization of second ionic state, which is most sensitive probe for rotational isomerism in case of simple vinyl compounds. It can be deduced from orbital energy dependence on changes of dihedral angles. For methyl vinyl ether and also for the corresponding thioether this method, in contrast to DFT/MRCI calculations [49] reveal that cis and gauche ($\vartheta = 45^\circ$) forms have almost the same energy (gauche is about 1 kcal/mol more stable). The main feature is characteristic for n – π conjugation. The closeness of energies of different rotamers in these molecules is not surprising, regarding the experimental support for a mixture of rotamers of vinyl alcohol [17] in gas phase. It is noteworthy that

Table 1

Ionization energies of some vinyl, allyl, and phenyl ethers, sulphides, and related compounds (the ionic states are labeled according to the designation of orbitals from which they arise, see text). Data labeled * are from this work. RHF/6-31G* eigenvalues are multiplied by 0.92

No.	Compound	Method	IE (eV)	Ref.
1.	H ₂ C=CHOH	PES	9.15 π (C=C–O) 9.30 13.69 n (O) 14.42 π (C=C–O) 16.88 σ (C–C,C–O) 19.50 σ (C–C,C–O)	[17] *
2.	H ₂ C=CHOCH ₃	PI	8.93	*
		PES	8.95 _a	*
			9.13 π 12.05 n 12.48 13.36 14.27 16.04 17.01?	[21]
		PES	9.05 π 12.0 n 12.5 13.3	[66]
		PES	9.14 π 12.10 n 12.40 π 13.40 14.30 16.00 18.70	[24]
3.	H ₂ C=CHOC ₂ H ₅	PI	8.83	*
		6-31G*	8.47 π (O,CC) 11.97 π CC 12.18 12.97 13.72 13.86	*
4.	H ₂ C=CHOC ₃ H _{7-n}	PI	8.75	*
		PES	8.64 _a	*
			8.86 π 11.39 n (O) 12.67 14.42 16.77	*
		6-31G*	8.45 π (O,CC) 11.80 π O 11.90 n O 12.57 σ 12.73 π CO 12.86 σ	*
		DFT	5.91 π (O,CC) 8.70 n O 8.95 9.39 π CH ₂ 9.45 σ 10.11 σ	*
5.	Cl ₂ C=CHOCH ₃	PES	8.46 _a	*
			8.84 π 11.39 n Cl 11.82 n Cl 12.04 n Cl 12.54 n O 13.99 14.78 16.72	*
		6-31G*	8.56 π (CC,O,Cl) 11.20 n Cl 11.77 n Cl 11.97 n Cl, σ CC 12.90 π	*
		DFT	6.21 π (CC,O,Cl) 8.49 n Cl 8.91 n Cl 9.05 n Cl, σ CC 9.66 π (O,CC)	*
6.	Cl ₂ C=CHOC ₂ H ₅	PES	8.36 _a	*
			8.78 π 11.39 n Cl 12.00 n Cl 13.24 n Cl 13.92 n O 14.82 16.77	*
		6-31G*	8.51 π (CC,O,Cl) 11.15 n Cl 11.72 π Cl 11.90 n Cl, n O 12.47 π	*
		DFT	6.16 π (CC,O,Cl) 8.43 n Cl 8.85 π Cl 8.98 n Cl, n O 9.40 π (O,Cl)	*
7.	Cl ₂ C=CHOCH(CH ₃) ₂	PI	8.14	*
8.	Cl ₂ C=CHOCH ₂ CH ₂ Cl	PES	8.44	*
			8.99 π 11.39 n Cl 12.05 n Cl 12.90 n Cl 14.25 n Cl 15.15	*
		6-31G*	8.79 π (CC,O,Cl) 11.19 π Cl 11.21 n Cl 11.39 n Cl 11.92 n Cl	*
		DFT	6.43 π (CC,O,Cl) 8.42 π Cl 8.49 n Cl 8.66 n Cl 9.06 π Cl 9.29 n Cl	*
9.	(H ₂ C=CH) ₂ O	PES	9.00 π 10.51 π 12.43 n O 12.60 π	[67] *
		6-31G*	8.34 π (O,CC) 9.73 π CC 12.78 σ 12.89 n O	*
		DFT	6.13 π (O,CC) 7.52 π CC 9.36 n O 9.83 σ CH 11.34 σ CH 11.66 σ	*
10.	H ₂ C=CHOC ₆ H ₅	PI	8.36	*
		PES	8.33 _a	*
			8.49 π 9.33 π 11.69 π 12.60 π 14.11 π 15.6 n O 17.5	*
		6-31G*	7.88 π O 8.54 π a_2 9.07 π CC 12.27 n O 12.36 σ CC 12.96 13.28 π	*
		DFT	5.94 π O 6.85 π a_2 7.18 π CC 8.97 n O 9.40 n O' 9.87 σ CC,CH	*
11.	H ₂ C=CHCH ₂ OH	PI	9.67	*
		PES	9.63 _a	*
			10.16 π 10.93 n 12.2 13.3 14.2 15.2 16.4 17.3 18.7	[60]
		PES	10.22 π 10.99 n 12.35 13.28 14.34? 15.30 17.32	[21]
12.	H ₂ C=CHCH ₂ OCH ₃	PES	9.84 π 10.34 n	[68]
13.	H ₂ C=CHCH ₂ OC ₂ H ₅	PI	9.62	*
		PES	9.41 _a	*
			9.60 π 10.18 n 11.44 12.20 13.31 14.56 16.48	*
		6-31G*	8.88 π CC 10.52 π O 11.81 n O 12.03 σ CC,CH 12.74 π CH ₂	*
		DFT	6.67 π (O,CC) 7.07 π (O,CC)) 8.62 n O 9.21 σ CC,CH 9.70 π CH ₂	*
14.	(H ₂ C=CHCH ₂) ₂ O	PI	9.48	*
		PES	9.44 _a	*
			9.64 π 10.13 π 11.54 n 12.69 13.68 14.51 16.64	*
		6-31G*	9.00 π CC 9.02 π CC 10.90 π O 11.87 σ CC 12.05 σ CC 13.17 σ	*
		DFT	6.65 π O 6.88 π CC 751 π (O,CC) 8.80 n O 9.24 σ CC,CH 9.96 σ	*
15.	H ₂ C=CHCH ₂ OC ₆ H ₅	PI	8.22	*

Table 1 (continued)

No.	Compound	Method	IE (eV)	Ref.
16.	HC \equiv CCH ₂ OH	PES	8.15 _a	*
			8.31 π 9.24 9.93 11.00 11.42 12.18 14.06 14.79 15.68 17.24	*
		6-31G*	7.65 π O 8.34 πa_2 9.21 π CC 11.39 n O 11.95 n O' 12.57 π 12.76 π	*
		DFT	5.86 π O 6.67 πa_2 7.14 π CC 8.45 n O 8.85 n O' 9.59 σ CC,CH	*
		PI	10.56	*
17.	ClCH ₂ OCH ₃	PES	10.59 10.92 11.53 13.40 16.26 17.51 18.58	*
		PES	10.5 π 10.9 π CC 11.5 n O 13.3 15.7 16.2 17.3 18.4 22.5 23.9	[69]
18.	ClCH ₂ CH ₂ OH	PES	10.90 11.30 11.56 12.83 14.35 14.73 16.33 17.20	*
		PI	10.52	*
19.	ClCH ₂ CH ₂ OCH ₃	PES	10.85	*
		PES	10.90 11.45 11.71 12.62 13.90 14.62 15.78 16.18 17.60	[70]
		PES	10.27 11.86 12.0	*
20.	C ₆ H ₅ OCH ₃	PES	8.42 π 9.23 π 11.02 n O 11.60 12.4	[71]
		PES	8.20	*
			8.44 9.23 11.04 11.53 12.39 13.99 14.87 15.62 17.29	*
		6-31G*	7.63 πb_1 ,O 8.37 πa_2 11.57 πb_1 ,O' 11.90 12.71 13.03 13.11	*
		DFT	5.85 πb_1 ,O 6.69 πa_2 8.57 πb_1 ,O' 8.76 n O, σ CC 9.60 σ CO,CC	*
21.	C ₆ H ₅ OCH ₂ CH ₃	PES	8.16	*
			8.36 9.25 10.89 11.38 12.06 14.03 15.32 17.37	*
		6-31G*	8.02 πb_1 ,O 8.37 πa_2 10.78 n O' 12.02 n O 12.43 σ CC,CH 12.45	*
		DFT	6.40 πb_1 ,O 6.75 πa_2 7.20 n O' 8.98 n O 9.43 σ CC,CH 9.64 σ CC	*
		PES	8.71 π 9.22 π 9.74 11.22 n O	[72]
22.	C ₆ H ₅ OC(CH ₃) ₃	PES	10.00 π 11.66 n Cl 12.16 n Cl 12.24 n Cl 12.55 π 13.84 n Cl	[73]
		PES	9.74 11.38 12.50 13.47	[74]
23.	Cl ₂ C=CH ₂	PES	8.45 n S 11.0 π 11.5 12.5 13.8 14.9	[66]
		PES	8.45 n 11.0 π 11.55 n S 12.6	[15]
		PES	8.44 π 11.0 n S 11.55 π 12.50 13.80 14.90 17.65	[24]
24.	H ₂ C=CHSCH ₃	PI	8.21	*
		PES	8.50 10.95 11.28	*
		6-31G*	8.09 π (S,CC) 9.93 π (CC,S) 11.18 n S 12.14 12.87 π CH ₃ 13.59 π	*
25.	H ₂ C=CHSC ₂ H ₅	PI	8.16	*
		PES	8.16 10.75	*
			8.34 10.79 11.15 11.87 12.45 15.2? 19.58	*
		6-31G*	7.78 π (S,CC) 10.77 π (CC,S) 10.97 n S 11.68 σ 12.30 12.46	*
		DFT	5.73 π (S,CC) 7.83 π (S,CC) 8.59 n S 9.21 σ CS,CC 9.41 σ CC,CH	*
26.	H ₂ C=CHSC ₃ H ₇	PI	8.15	*
		PES	8.15	*
27.	H ₂ C=CHSCH(CH ₃) ₂	PI	8.07	*
		PES	7.92 _a	*
			8.33 10.19 11.5 13.5 15.1	*
28.	H ₂ C=CHC ₄ H ₉	6-31G*	8.11 π (S,CC) 9.53 n S 11.0 π (CC,S) 11.54 σ CS,CC 12.04 σ CC	*
		DFT	5.69 π (S,CC) 8.11 n S 8.26 π (CC,S) 8.78 σ CH,CC 9.39 σ CC,CH	*
		PI	8.25	*
		PES	8.22 10.23	*
			8.44 10.35 11.38 11.88 12.48 13.90	*
29.	(H ₂ C=CH) ₂ S	PES	8.42	[74]
		6-31G*	7.66 π (S,CC) 9.92 π CC 11.41 n S 11.98 π S 12.01 σ 14.34 σ	*
		DFT	5.81 π (S,CC) 7.69 π CC 8.97 n S, σ CC 9.32 σ CH,CS 9.39 π S	*
		PI	7.96	*
		PES	7.86 9.22 10.63	*
30.	H ₂ C=CHSC ₆ H ₅		8.27 9.39 9.77? 10.94 11.49 11.99 12.36 13.38 14.25 14.99	*
			16.62 17.92 19.43	*
		6-31G*	7.73 π Sb ₁ 8.51 πa_2 8.94 π S,CCb ₁ 10.78 π CC,S 11.46 n S 12.28	*

Table 1 (continued)

No.	Compound	Method	IE (eV)	Ref.
32.	H ₂ C=CHCH ₂ SH	DFT	5.73πS 6.94πa ₂ 7.26πCCbb ₁ 8.32πCC,S 8.93nS 9.48σCC,CH	*
33.	H ₂ C=CHCH ₂ SCH ₃	PES	9.25n _S 10.05π 11.9 12.7 13.6 14.6 15.1 16.2 18.4	[61]
34.	H ₂ C=CHCH ₂ SC ₂ H ₅	PI	8.51	*
		PES	8.40 9.65 10.53 11.52	*
			8.50n _S 9.89 10.85 12.06 12.61 13.67? 14.77	*
		6-31G*	8.32πS 9.11πCC 10.69nS 11.92σCC,CS 12.64σ 12.84σ	*
		DFT	5.89πS 7.03πCC 8.33nS 9.33σCS,CC 9.69σCH 9.91σCH	*
35.	H ₂ C=CHCH ₂ SCH ₂ Cl	PES	8.72 9.09 10.35 11.27 12.12 12.88 13.97 15.00	*
36.	CH ₃ SCH ₂ Cl	PES	9.24nS 11.09nCl 12.10 12.32? 13.15 13.50 13.90 14.8	*
37.	C ₃ H ₇ SCH ₂ Cl	PES	9.05nS 11.03nCl 11.50 12.05 12.70 13.20	*
38.	(H ₂ C=CHCH ₂) ₂ S	PI	8.52	*
		PES	8.44	*
			8.55 9.75 11.05 12.3 13.7 14.7	*
		PES	8.43 9.5 10.82 11.8	*
			8.60 9.82 10.02 11.15	[75]
		6-31G*	8.36πS 9.15πCC 9.37πCC 10.87nS 12.00σCS,CC 12.64σ	*
		DFT	5.97πS 7.02πCC 7.19πCC 8.55nS 9.37σCC,CH 9.80σCS	*
39.	H ₂ C=CHCH ₂ SC ₆ H ₅	PI	7.91	*
		PES	7.77	*
			8.13 8.49 9.23 9.84 11.00 11.83 14.03 14.84 16.61	*
		6-31G*	8.31πS 8.47πa ₂ 8.58nS 9.26πCC 11.03nS' 12.14σCS,CC	*
		DFT	6.02nS 6.83πS 6.97πa ₂ 7.20πCC 8.69σCS 9.52σCC,CH	*
40.	(ClCH ₂ CH ₂) ₂ S	PES	8.51 8.77 10.53	*
			8.60 9.11 11.17 11.72 12.60 13.76 14.54 16.48	*
		6-31G*	9.03nS 10.91nCl 11.09nCl 11.10nCl 11.10nCl 11.51nS	*
41.	(C ₆ H ₅) ₂ S	PI	7.92	*
42.	C ₆ H ₅ SCH ₃	PI	7.96	*
		PES	8.07π 9.28π 10.14nS 11.1 11.9	[76]
		PES	7.96 9.15 9.78	*
			8.12 9.33 10.09 11.07 11.92 13.41 14.06 14.90 16.71	*
		6-31G*	8.37πbb ₁ 8.47πa ₂ 8.59nS 10.01 12.17 12.51 13.02 13.90	*
		DFT	5.63πbb ₁ ,S 6.81πa ₂ 7.71πbb ₁ ,S' 8.63nS 9.35σCC,CH 9.73	*
43.	C ₆ H ₅ SCH ₂ CH ₃	PI	7.88	*
		PES	7.86	*
			8.01 8.44 9.24 10.00 10.88 11.65 12.19 14.04 14.85 16.59	*
		6-31G*	8.33πbb ₁ 8.44πa ₂ ,S 8.55nS' 10.91nS 11.79σCC,CS 12.48σ	*
		DFT	6.04nS' 6.75πbb ₁ 6.91πa ₂ 8.50nS 9.21σCC,CS 9.47σCC,CH	*

SCF/6-31G* calculations do not reproduce the experimentally established cis conformation of the methyl vinyl ether and sulphide. The same holds for other alkyl substitutions, whereas DFT supports cis conformations as the most stable for all alkyl substituents (even for bulky tert-butyl group). The only exception is the propyl group. As noted in Ref. [60], the conformer composition stays still under discussion while the results of different experimental methods are inconsistent.

Resonance interactions between orbitals of the

same symmetry and inductive interactions caused by electronegativity differences in these systems are not always in the same direction as those of the vinyl compounds. In allyl compounds the difference is due to the linking of alkyl group to CH₂, which can cause shifts in the inherent energies of the *n* and *π* orbitals [61]. The *π*-orbital contains some *σ*-bond orbital character in an antibonding combination, the chemists call this effect hyperconjugation and it appears in orbital scheme as a *σ*–*π* mixing.

The spectrum of allyl alcohol exhibits at least nine

Table 2

The main features of geometry of vinyl, allyl and phenyl ethers and sulphides predicted by HF/6-31G*. Some remarks are made on DFT results (note: in vinyl and allyl compounds the numeration of atoms starts from terminal carbon of vinyl group, in phenyl alkyl compounds the numeration starts from terminal carbon atom of alkyl group)

Compound	E_{tot} , a.u.	Geometry
1. $(\text{CH}_2=\text{CH})_2\text{O}$	– 229.75355	C_{2v} : $\text{COC}=129^\circ$, $\text{C1C2}=1.318 \text{ \AA}$, $\text{C1O}=1.351 \text{ \AA}$
2. $\text{CH}_2\text{CHOCH}_2\text{CH}_3$	– 230.95592	planar, trans: $\text{COC}=118.7^\circ$, $\text{C1C2}=1.321 \text{ \AA}$, $\text{C2O}=1.341 \text{ \AA}$, $\text{OC3}=1.406 \text{ \AA}$; DFT: cis
3. $\text{CH}_2=\text{CHOC}_3\text{H}_7-n$	– 269.99065	planar, trans: $\text{COC}=118.1^\circ$, $\text{C1C2}=1.321 \text{ \AA}$, $\text{C2O}=1.341 \text{ \AA}$, $\text{OC3}=1.405 \text{ \AA}$; DFT: trans
4. $\text{Cl}_2\text{C}=\text{CHOCH}_3$	– 1109.69717	planar, cis: $\text{COC}=124.3^\circ$, $\text{C1C2}=1.323 \text{ \AA}$, $\text{C2O}=1.327 \text{ \AA}$, $\text{OC3}=1.412 \text{ \AA}$; DFT: cis
5. $\text{Cl}_2\text{C}=\text{CHOC}_2\text{H}_5$	– 1148.73750	planar, cis: $\text{COC}=124.8^\circ$, $\text{C1C2}=1.324 \text{ \AA}$, $\text{C2O}=1.327 \text{ \AA}$, $\text{OC3}=1.420 \text{ \AA}$; DFT: cis
6. $\text{Cl}_2\text{C}=\text{CHOCH}_2\text{CH}_2\text{Cl}$	– 1607.63630	planar, cis: $\text{COC}=124.9^\circ$, $\text{C1C2}=1.322 \text{ \AA}$, $\text{C2O}=1.332 \text{ \AA}$, $\text{OC3}=1.414 \text{ \AA}$; DFT: cis
7. $\text{CH}_2=\text{CHSC}_2\text{H}_5$	– 553.61242	gauche, $\vartheta = 49^\circ$: $\text{CSC}=100^\circ$, $\text{C1C2}=1.318 \text{ \AA}$, $\text{C2S}=1.769 \text{ \AA}$, $\text{SC3}=1.822 \text{ \AA}$; DFT: planar, cis
8. $\text{CH}_2=\text{CHSC}_3\text{H}_7$	– 592.64760	planar, cis: $\text{CSC}=103.4^\circ$, $\text{C1C2}=1.320 \text{ \AA}$, $\text{C2S}=1.761 \text{ \AA}$, $\text{SC3}=1.815 \text{ \AA}$; DFT: planar, trans
9. $\text{CH}_2=\text{CHSC}_4\text{H}_9-t$	– 631.68087	gauche, $\vartheta = 60^\circ$: $\text{CSC}=104^\circ$, $\text{C1C2}=1.319 \text{ \AA}$, $\text{C2S}=1.772 \text{ \AA}$, $\text{SC3}=1.851 \text{ \AA}$; DFT: cis
10. $(\text{CH}_2=\text{CH})_2\text{S}$	– 552.40949	C_{2v} : $\text{CSC}=112.7^\circ$, $\text{C1C2}=1.319 \text{ \AA}$, $\text{C2S}=1.762 \text{ \AA}$
11. $\text{CH}_2=\text{CHCH}_2\text{OC}_2\text{H}_5$	– 269.98489	planar, cis: $\text{COC}=114.6^\circ$, $\text{C1C2}=1.317 \text{ \AA}$, $\text{C2C3}=1.501 \text{ \AA}$, $\text{C3O}=1.39 \text{ \AA}$, $\text{OC4}=1.397 \text{ \AA}$; DFT: cis
12. $(\text{CH}_2=\text{CHCH}_2)_2\text{O}$	– 307.82020	C_{2v} : $\text{COC}=114.4^\circ$, $\text{C1C2}=1.317 \text{ \AA}$, $\text{C2C3}=1.508 \text{ \AA}$, $\text{OC3}=1.396 \text{ \AA}$
13. $\text{CH}_2=\text{CHCH}_2\text{SC}_2\text{H}_5$	– 592.64710	gauche, $\vartheta = 60^\circ$, allyl plane: $\text{CSC}=100^\circ$, $\text{C1C2}=1.318 \text{ \AA}$, $\text{C2C3}=1.502 \text{ \AA}$, $\text{C3S}=1.824 \text{ \AA}$, $\text{SC4}=1.818 \text{ \AA}$; DFT: gauche, $\vartheta = 90^\circ$.
14. $(\text{CH}_2=\text{CHCH}_2)_2\text{S}$	– 630.47971	C_{2v} : $\text{CSC}=99.8^\circ$, $\text{C1C2}=1.317 \text{ \AA}$, $\text{C2C3}=1.514 \text{ \AA}$, $\text{SC3}=1.817 \text{ \AA}$
15. $\text{CH}_2=\text{CHOC}_6\text{H}_5$	– 382.43036	bend, phenyl plane 45° to vinyl: $\text{COC}=118.8^\circ$, $\text{C1C2}=1.314 \text{ \AA}$, $\text{C2O}=1.358 \text{ \AA}$, $\text{OC3}=1.363 \text{ \AA}$; DFT: similar structure
16. $\text{CH}_2=\text{CHCH}_2\text{OC}_6\text{H}_5$	– 421.46162	bend, phenyl plane 90° to vinyl: $\text{COC}=120.8^\circ$, $\text{C1C2}=1.317 \text{ \AA}$, $\text{C2C3}=1.505 \text{ \AA}$, $\text{C3O}=1.402 \text{ \AA}$, $\text{OC4}=1.355 \text{ \AA}$; DFT: similar structure
17. $\text{CH}_2=\text{CHSC}_6\text{H}_5$	– 705.08754	bend, $\vartheta = 60^\circ$: $\text{CSC}=101^\circ$, $\text{C1C2}=1.318 \text{ \AA}$, $\text{C2S}=1.772 \text{ \AA}$, $\text{SC3}=1.787 \text{ \AA}$; DFT: similar structure
18. $\text{CH}_2=\text{CHCH}_2\text{SC}_6\text{H}_5$	– 744.12233	bend, phenyl plane 90° to vinyl: $\text{CSC}=102^\circ$, $\text{C3S}=1.82 \text{ \AA}$, $\text{SC4}=1.787 \text{ \AA}$; DFT: similar
19. $\text{C}_6\text{H}_5\text{SCH}_2\text{CH}_3$	– 706.28078	gauche, $\vartheta = 90^\circ$: $\text{CSC}=101^\circ$, $\text{C2S}=1.826 \text{ \AA}$, $\text{SC3}=1.787 \text{ \AA}$, $\text{C1C2}=1.526 \text{ \AA}$; DFT: similar
20. $\text{C}_6\text{H}_5\text{OCH}_2\text{CH}_3$	– 383.62145	gauche, $\vartheta = 90^\circ$: $\text{COC}=115.8^\circ$, $\text{C2O}=1.412 \text{ \AA}$, $\text{OC3}=1.363 \text{ \AA}$; DFT: similar
21. $\text{C}_6\text{H}_5\text{SCH}_3$	– 667.24528	gauche, $\vartheta = 90^\circ$: $\text{CSC}=101^\circ$, $\text{C1S}=1.816 \text{ \AA}$, $\text{SC2}=1.787 \text{ \AA}$; DFT: planar
22. $\text{C}_6\text{H}_5\text{OCH}_3$	– 344.58326	planar: $\text{COC}=119.8^\circ$, $\text{C1O}=1.398 \text{ \AA}$, $\text{OC2}=1.350 \text{ \AA}$; DFT: similar
23. $\text{CH}_2=\text{CHOCH}_3$	– 191.91272	planar, trans: $\text{COC}=116.4^\circ$, $\text{C1C2}=1.316 \text{ \AA}$, $\text{C2O}=1.348 \text{ \AA}$, $\text{OC3}=1.399 \text{ \AA}$; DFT: planar, cis
24. $\text{CH}_2=\text{CHSCH}_3$	– 514.57591	planar, trans: $\text{COC}=101^\circ$, $\text{C1C2}=1.318 \text{ \AA}$, $\text{C2S}=1.769 \text{ \AA}$, $\text{SC3}=1.810 \text{ \AA}$; DFT: planar, cis

ionization bands below 21 eV. The first band is attributed to ionization of a $\pi(\text{C}=\text{C})$ electron while the relatively sharp second band is of n_{O} character. Resonance interactions in allyl ethers are very small due to the large energy difference between the $\pi(\text{C}=\text{C})$ and n_{O} of the substituent. For example, the $\pi(\text{C}=\text{C})$ in $\text{H}_2\text{C}=\text{CHCH}_2\text{OH}$ is stabilized by 0.28 eV, while the n_{O} is destabilized by only 0.05 eV when compared to propylene and methyl alcohol, respectively [61]. The resonance effect appears to be of minor importance compared to the strong inductive effect by which electron density is drawn toward the electronegative

O atom, thereby stabilizing the $\pi(\text{C}=\text{C})$ orbital. The π orbital of the vinyl group becomes delocalized over a large portion of the molecule whereas the nonbonding orbital acquires more bonding character.

Even though both calculation methods used yield the planar geometry of heavy atom skeleton in cis form, a certain discrepancy between them exists in orbital population. Whereas DFT predicts a bonding and antibonding π -combinations of oxygen and vinyl group orbitals a highest orbitals, the HF does not mix these orbitals at all.

In the spectrum of allyl methyl sulphide [62] bands

1 (8.6 eV) and 3 (11.15 eV) appear at essentially the same positions as the uppermost bands in dimethyl sulphide. As in both compounds the character of sulfur lone pairs is very similar. One assigns band 1 to the $n(\pi)$ MO (perpendicular to CSC plane) and band 3 to the $n(\sigma)$ MO (in the CSC plane). Our calculations of allyl ethyl sulphide employing HF and DFT methods support this assignment perfectly. The delocalization of the second IP was not found by this calculation. Vinyl $\pi(\text{C}=\text{C})$ orbital occurs to be fully localized in allyl ethyl sulphide though somewhat destabilized as compared to ethene (0.6 eV). This band was assigned to be an antibonding combination of the ethene π -MO and the neighboring σ -MO-s of the CH_2SCH_3 substituent. Downward shift relative to the first band of ethene (10.5 eV) was expected to be a measure of the importance of σ - π mixing which depends on the conformation of the molecule. In the PES of propene we can find the downward shift of 0.6 eV through C-H mixing. As shown [63] the hyperconjugative abilities of C-S and C-H bonds are nearly equal and the stabilizing inductive effect due to the SAlk group is small.

Indeed, allyl sulphide $\text{CH}_2\text{CHCH}_2\text{SH}$ is known experimentally to exist only in the gauche form [64] where C-S hyperconjugation is possible. The situation is perfectly reproduced by our calculations (the HF/6-31G* produces the gauche form $\vartheta = 60^\circ$, whereas DFT most stable conformation is SEt group perpendicular to the vinyl plane). However, the population analysis does not reveal any impression of orbital mixing. Apparently, such notations as symmetry orbitals $\pi(\text{C}=\text{C})$ or πS (see Table 1) do not apply to these molecules. Instead, these notations refer to the orbital perpendicular to vinyl plane and to an orbital localized on sulfur atom coplanar to this plane (perpendicular to CSC plane), respectively.

Diallyl ether and sulphide appear to be both of C_{2v} symmetry. In diallyl sulphide the highest occupied MO is n_{S} . In contrast to the HF calculation the DFT predicts also the n_{O} orbital energy higher as π orbitals of C=C bond.

In benzene, the lowest ionization 9.25 eV is due to ionization from the $\pi(\text{e}_{1g})$ orbital. In monosubstituted benzenes (C_{2v} or lower symmetry) this MO is split into two orbitals, one having a π -interaction with the substituent (b_1 in C_{2v}) and another not interacting (a_2 in C_{2v}). The separation between these two levels is

the greatest with the substituents with polarizable lone pairs. So, the replacement of one H atom in benzene by a SH group has an enormous effect [65] of 2.37 eV as calculated from the difference between the first band (8.28 eV) and third band (10.85 eV) energies. This effect reduces in the regular way: SMe 1.97 eV and SEt 1.23 eV. The same effect for oxygen containing groups is even more impressive: OH 3.0 eV, OMe 2.6 eV, and OEt 2.53 eV.

Phenyl methyl ether is calculated to be the most stable in form $\vartheta = 0^\circ$ and the orbital population corresponds to the considerations above. Of course, the above described model fails in the case of SMe, OEt, and SEt substitution as they are calculated to be stable at $\vartheta = 90^\circ$. The identities of the a_2 and the substituent n and π orbitals are thus masked by the presence of σ orbitals which begin to appear in this region.

Both HF and DFT methods used in this work state that in vinyl phenyl ethers and sulphides exist in bent form where the angle between vinyl and phenyl planes is about 45 and 60°, respectively. Allyl phenyl ethers and sulphides tend to be in form with benzene ring plane and vinyl (allyl group is planar) plane perpendicular to each other.

4. Conclusions

DFT calculations can be applied for quite large molecules with different substituents. In most cases, the KS orbitals exhibit the same main feature as MO-s. The correlation KS orbital energy vs experimental ionization energies is linear with a slope almost 1.0, but the intercept is nearly 2 eV.

In molecules containing structural groups with developed π -system, the unambiguous assignment of orbitals is very complicated as the molecules have many rotamers and the ground state geometry is not very clear. In some cases the DFT and HF method predict different geometry for ground state of a molecule.

As follows from Table 1, the DFT/B3LYP (using 6-31G* basis set) orbital energies are, in all cases, calculated to be more than 2 eV too low compared to experimental ionization energies. This is in crude contrast to our previous model of two main contributions to orbital energies: electron correlation energy

difference and cation orbital reorganization. In our calculations, we expected rather contradictory effect regarding that in DFT calculations only the ground-state electron correlation contribution is taken in account. Possibly, it can be explained by the use of B3LYP functional, which, as noted above, is really a hybride one. It seems necessary to expand calculation of PES with the use of different functionals.

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