

The Electronic Structure of Molecules by a Many-Body Approach

VIII. Ionization Potentials of the Three-Membered Ring Molecules C_3H_6 , C_2H_4O , C_2H_5N

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The vertical valence ionization potentials of cyclopropane, ethylene oxide and ethylene imine are calculated by a many-body Green's function method. For C_3H_6 the ordering of the ionization potentials is $2e'(\sigma)$, $1e''(\pi)$, $2a'_1(\sigma)$, $1a''_2(\pi)$, $1e'(\sigma)$. The assignment of the $2a'_1$ and the $1a''_2$ ionization potentials which has been controversial is thus clarified. The ordering is in agreement with the result obtained via Koopmans' theorem. For ethylene oxide and ethylene imine Koopmans' theorem fails in predicting the correct order of ionic states. For C_2H_4O the ordering of the ionization potentials is $2b_1(\pi)$, $4a_1$, $1a_2(\pi)$, $2b_2$, $3a_1$, $1b_1(\pi)$, $1b_2$, $2a_1$ and for C_2H_5N $6a'$, $5a'$, $3a''$, $2a''$, $4a'$, $3a'$, $1a''$, $2a'$. The agreement of the computed ionization potentials with the experimental values is very satisfactory.

Key words: C_3H_6 ring molecule, ionization potential of \sim - C_2H_4O ring molecule, ionization potential of \sim - C_2H_5N ring molecule, ionization potential of \sim

1. Introduction

The photoelectron spectrum (PES) of cyclopropane has been investigated by Turner *et al.* [1, 2] and Lindholm *et al.* [3] and those of ethylene oxide and ethylene imine by Turner *et al.* [1, 2]. The spectra have been assigned on the basis of *ab initio* SCF calculations by Basch *et al.* [2]. In several cases reorganization effects and an estimate of correlation effects have been included. The ordering of ionic states supplied by Koopmans' theorem [4] was considered to be correct except for the ordering of the two first ionization potentials (IP's) of ethylene oxide which were accidentally degen-

erate in the calculation. In a later paper Evans *et al.* [5] argued that the ordering of the third and fourth IP's of cyclopropane should be reversed with respect to the *ab initio* SCF calculation which would lead to a more reasonable explanation of the vibrational structure and intensity of the corresponding bands. Numerous calculations have been performed on the three molecules and in particular on cyclopropane [2, 3, 6-9] (for a list of references see Ref. [6]) and practically all agree on the ordering of the IP's derived via Koopmans' theorem.

In the present work calculations of the vertical valence IP's of the three molecules are presented which include the effect of electron correlation and reorganization. The IP's are calculated directly by a many-body Green's function method [10]. The results of these calculations are presented in the subsequent section. Satellite lines are not considered in this article. They can be calculated by the method presented in Ref. [19].

2. Results for the Ionization Potentials

The *ab initio* SCF calculations on which the Green's function calculations are based have been performed with the program system MUNICH [11]. The molecular orbitals (MO's) are expanded in a basis set of Cartesian Gaussian functions of double-zeta

Table 1. Total SCF energies (in a.u.) and orbital energies (in eV) for C₃H₆, C₂H₄O and C₂H₅N^a

| C ₃ H ₆ | | C ₂ H ₄ O | | C ₂ H ₅ N | | | |
|---------------------------------|-------------|---------------------------------|-------------|---------------------------------|-------------|-------------|---------|
| Basis (9s5p/4s) | | Basis (9s5p1d/4s) | | Basis (9s5p1d/4s) (11s7p/6s1p) | | | |
| $E_{\text{tot}}^{\text{SCF}} =$ | -116.983528 | $E_{\text{tot}}^{\text{SCF}} =$ | -152.840726 | $E_{\text{tot}}^{\text{SCF}} =$ | -133.011963 | -133.021566 | |
| a'_1 | -306.03 | a_1 | -559.84 | a' | -423.60 | a' | -423.72 |
| e' | -306.01 | a_1 | -307.50 | a' | -306.64 | a' | -306.56 |
| | | b_2 | -307.48 | a'' | -306.62 | a'' | -306.54 |
| $1a'_1(\sigma)$ | -30.96 | $1a_1$ | -37.93 | $1a'$ | -34.03 | $1a'$ | -34.73 |
| $1e'(\sigma)$ | -22.10 | $2a_1$ | -25.19 | $2a'$ | -24.23 | $2a'$ | -24.52 |
| | | $1b_2$ | -23.43 | $1a''$ | -22.74 | $1a''$ | -22.92 |
| $1a''_2(\pi)$ | -18.30 | $1b_1(\pi)$ | -19.23 | $3a'$ | -19.05 | $3a'$ | -19.18 |
| $2a''_1(\sigma)$ | -17.00 | $3a_1$ | -17.93 | $4a'$ | -17.37 | $4a'$ | -17.38 |
| $1e''(\pi)$ | -13.94 | $1a_2(\pi)$ | -14.97 | $2a''$ | -14.49 | $2a''$ | -14.55 |
| | | $2b_2$ | -14.83 | $5a'$ | -13.09 | $5a'$ | -13.16 |
| $2e'(\sigma)$ | -11.50 | $4a_1$ | -12.34 | $3a''$ | -13.03 | $3a''$ | -13.07 |
| | | $2b_1(\pi)$ | -12.31 | $6a'$ | -10.76 | $6a'$ | -10.69 |
| Virtual orbitals | | | | | | | |
| $3a''_1(\sigma)$ | 5.26 | $5a_1$ | 5.15 | $7a'$ | 4.85 | $4a''$ | 2.81 |
| $2a''_2(\pi)$ | 5.94 | $3b_2$ | 5.77 | $8a'$ | 5.73 | $7a'$ | 3.00 |
| $3e'(\sigma)$ | 6.25 | $6a_1$ | 6.28 | $4a''$ | 5.99 | $8a'$ | 3.68 |
| $1a''_2$ | 7.67 | $3b_1(\pi)$ | 6.83 | $9a'$ | 6.71 | $9a'$ | 4.59 |
| $2e''(\pi)$ | 8.60 | $4b_2$ | 7.01 | $5a''$ | 7.55 | $5a''$ | 5.50 |
| $4e'(\sigma)$ | 9.33 | $2a_2(\pi)$ | 8.15 | $6a''$ | 8.41 | $10a'$ | 5.97 |
| | | $5b_2$ | 9.34 | $10a'$ | 8.51 | $6a''$ | 6.73 |

^a The numbering of the orbitals starts with the first valence orbital.

quality: $(9s5p/4s)/[4s2p/2s]$ with exponential parameters and contraction coefficients taken from the work of Huzinga [12]. For ethylene oxide a further calculation has been performed with a basis set containing d -type polarization functions on the C and O atoms. Otherwise the basis is identical to the one mentioned above. The exponential parameters of the d -type functions are $\alpha_d(\text{C}) = 0.6$ and $\alpha_d(\text{O}) = 0.8$. For ethylene imine two additional calculations have been performed with larger basis sets: $(11s7p/6s1p)/[5s3p/3s1p]$ with parameters taken from the work of Salez and Veillard [13] and $(9s5p1d/4s)/[4s2p1d/2s]$ with $\alpha_d(\text{C}) = 0.6$ and $\alpha_d(\text{N}) = 0.65$. For C₃H₆ the geometry determined by Bastiansen *et al.* [14], for C₂H₄O the geometry determined by Cunningham *et al.* [15] and for C₂H₅N the one determined by Bak and Skaarup [16] has been used. The results for the orbital energies and the total SCF energies are listed in Table 1. For ethylene oxide and ethylene imine the results obtained with the larger basis sets are given (for ethylene imine there are two sets of results).

2.1. Cyclopropane

The results for the valence IP's obtained from the Green's function calculation are presented in Table 2 and are plotted in Fig. 1 together with the PES of Turner *et al.* [1]. The table contains the IP's in Koopmans' approximation, in second and third order of the perturbation expansion (IP⁽²⁾, IP⁽³⁾) the final results including renormalization (IP^(R)) together with the corresponding pole strengths ($P^{(R)}$) and the experimental maxima of the bands. The results of the calculations (vertical IP's) should be compared with the centroids of the bands [17], but these cannot in general be unambiguously derived from the spectrum. The pole strengths, P_i , also have a physical meaning. In the Hartree-Fock approximation the pole strength is unity for the simple ionization process and zero for the process of ejection of one electron and simultaneous excitation of another electron to unoccupied orbitals. When many-body effects are included, the P_i are less than unity for the simple ionization process and $1 - P_i$ gives the probability for satellite lines due to excitations accompanying photoionization. It is seen that all pole strengths (for all molecules considered here) are between 0.87 and 0.93, i.e. one may expect satellite lines in the PES of these molecules with about 7% to 13% of the intensity of the principal valence lines.

Table 2. Final results for the vertical valence IP's of cyclopropane (in eV)

| Symmetry | $-\epsilon_i^{\text{SCF}}$ | IP ⁽²⁾ | IP ⁽³⁾ | IP ^(R) | $P^{(R)}$ | IP (exp) ^a |
|----------------------------|----------------------------|-------------------|-------------------|-------------------|-----------|-----------------------------------|
| $2e'(\sigma_{\text{ext}})$ | 11.50 | 10.03 | 10.87 | 10.68 | 0.92 | 10.55 + 11.25 (10.9) ^b |
| $1e''(\pi)$ | 13.94 | 12.42 | 13.05 | 12.96 | 0.93 | 13.0 ^b |
| $2a'_1(\sigma)$ | 17.00 | 15.09 | 15.93 | 15.65 | 0.92 | 15.7 ^b |
| $1a''_2(\pi)$ | 18.30 | 16.34 | 17.07 | 16.84 | 0.91 | 16.7 ^b |
| $1e'(\sigma)$ | 22.90 | 19.65 | 20.31 | 20.11 | 0.89 | 19.5 (19.7) ^c |

^a Maxima of the bands with centroids given in brackets.

^b Ref. [1]. ^c Refs. [3, 5].

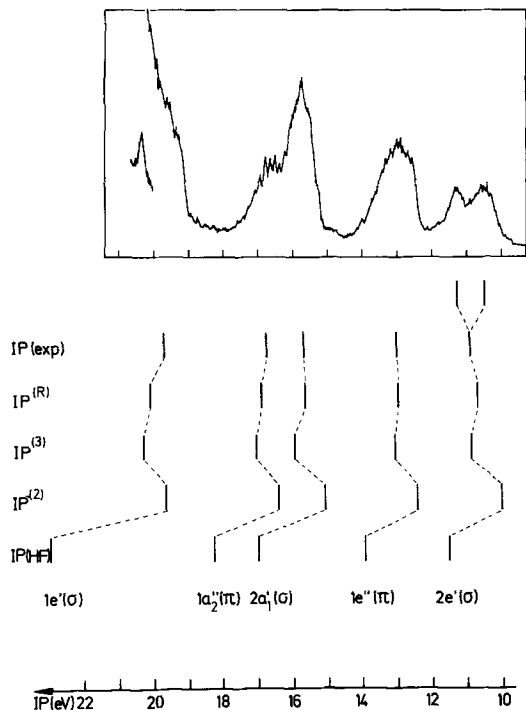


Fig. 1. Photoelectron spectrum of cyclopropane from Ref. [1] and calculated ionization potentials in different orders of the perturbation expansion

The first band which is due to the $2e'(\sigma)$ IP shows strong Jahn-Teller splitting with the two maxima at 10.55 and 11.25 eV and a centroid at about 10.9 eV. This value compares favourably with the value of 10.68 eV obtained for the centroid from the present calculation. The other two e -IP's ($1e''(\pi)$ at 13.0 eV and $1e'(\sigma)$ at about 19.5 eV) show little sign of Jahn-Teller distortion. It should be noted that the $1e'$ IP appears in Turner's first HeI spectrum at 20.3 eV but is in fact located at about 19.5 eV [3, 5]. The third and fourth bands at 15.7 and 16.7 eV show a rather peculiar intensity ratio when measured with the HeI line at 21.21 eV or the HeII line at 40.8 eV [1, 3, 5]. In the HeI spectrum the third band has the larger intensity than the fourth band, whereas in the HeII spectrum the reverse is true. The third band is probably distorted by autoionization in the HeI spectrum. In Koopmans' approximation the third band is assigned to the $2a_1'(\sigma)$ IP and the fourth band to the $1a_2''(\pi)$ IP in agreement with earlier studies [2]. Including many-body effects in the calculation of the IP's does not change the ordering. The original assignment of Basch *et al.* [2] is thus seen to be correct. The agreement of the computed with the experimental values is very satisfactory. All computed IP's are within 0.2 eV of the experimental value except for the $1e'$ IP. The centroid of the $1e'$ band is estimated to be at 19.7 eV. The error in the computed IP is thus 0.4 eV.

2.2 Ethylene Oxide

The results of the many-body calculation which employs the larger basis set are presented in Table 3 and Fig. 2 where again the spectrum of Turner *et al.* [1] is plotted.

Table 3. Final results for the vertical valence IP's of ethylene oxide (in eV)

| Symmetry | $-\epsilon_i^{\text{SCF}}$ | IP(2) | IP(3) | IP(R) | $\rho(\text{R})$ | IP (exp) |
|-------------|----------------------------|--------------------|--------------------|--------------------|------------------|----------|
| $2b_1(\pi)$ | 12.31 | 8.97 | 11.40 | 10.59 | 0.91 | 10.57 |
| $4a_1$ | 12.34 | 10.74 | 11.93 | 11.64 | 0.92 | 11.7 |
| $1a_2(\pi)$ | 14.97 | 13.65 | 13.96 | 13.88 | 0.93 | 13.7 |
| $2b_2$ | 14.82 | 12.80 | 14.43 | 14.07 | 0.91 | 14.2 |
| $3a_1$ | 17.93 | 15.51 | 16.96 | 16.42 | 0.91 | 16.6 |
| $1b_1(\pi)$ | 19.23 | 16.98 | 17.93 | 17.48 | 0.90 | 17.4 |
| $1b_2$ | 23.42 | 20.89 ^a | 21.50 ^a | 21.28 ^a | 0.88 | — |
| $2a_1$ | 25.19 | 21.69 ^a | 22.93 ^a | 22.48 ^a | 0.87 | — |

^a These values cannot be very accurate as satellite lines are lying in this energy range (see text).

As in previous investigations it is found that the $2b_1(\pi)$ and $4a_1$ IP's are accidentally degenerate in the Hartree-Fock calculation. (Note that we have reversed the b_1 and b_2 symmetry labels with respect to the work of Basch *et al.* [2].) Including many-body effects lifts this degeneracy and the $2b_1(\pi)$ IP is found at lower binding energy. The splitting between the two IP's is about 1 eV in good agreement with the experimental value of 1.1 eV.

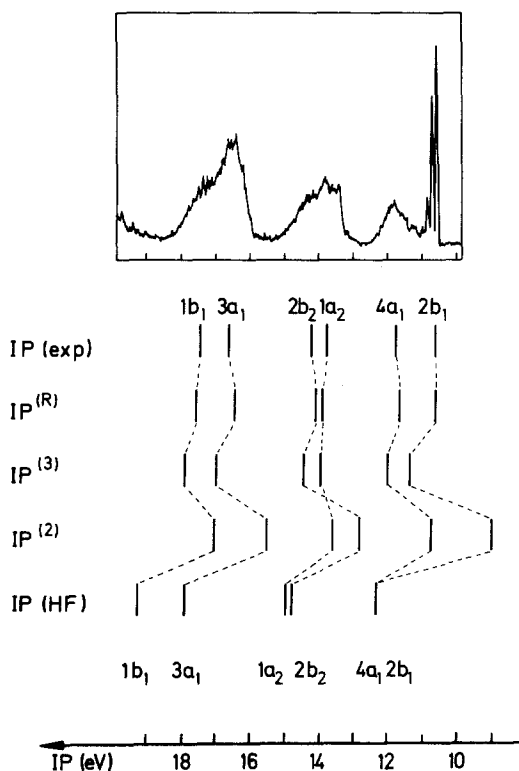


Fig. 2. Photoelectron spectrum of ethylene oxide from Ref. [1] and calculated ionization potentials in different orders of the perturbation expansion

The third band system contains the $2b_2$ and $1a_2(\pi)$ IP's. When the smaller basis set was used in the calculations it turned out that the $2b_2$ IP was smaller than the $1a_2$ IP according to the application of Koopmans' theorem and in the second-order calculation. In third order their sequence was reversed. The renormalization procedure led to identical values for both IP's. This coincidence is probably due to basis set effects. Thus d -type polarization functions were added to the basis and all IP's computed again. The values of the IP's are in general improved and the ordering of the IP's in the third band system appears to be clarified. The orbital energies of the $2b_2$ and $1a_2$ orbitals have come closer to each other. The ordering according to Koopmans' theorem and in the second-order calculation is again the same. In third order there is a change of ordering of the IP's which is maintained in the calculation involving renormalization: the $1a_2$ IP is smaller than the $2b_2$ IP. Koopmans' theorem thus fails to predict the correct ordering of states in this case.

The fourth band contains two IP's as well, the $3a_1$ and the $1b_1(\pi)$ IP. The $1b_2$ and $2a_1$ IP's have also been calculated but have not been measured so far. Except for the ordering of the $2b_2$ and $1a_2$ IP's the ordering of the IP's obtained by the many-body calculation agrees with the earlier study of Basch *et al.* [2] and also with the work of Chong *et al.* [18] who performed INDO calculations including first-order configuration interaction. All the IP's computed in this work are in good agreement with the experimental values, the maximum error is 0.2 eV. The two IP's which have been calculated but have not been measured so far ($1b_2$ and $2a_1$) cannot be very accurate as satellite lines are lying in their energy range. The renormalization method used in this work is then not justified and the more general method of Ref. [19] should be used.

2.3. Ethylene Imine

The *ab initio* SCF calculations on ethylene imine by Basch *et al.* [2] which formed the basis for the assignment of the PES were performed in the older geometry determined by Turner *et al.* [20]. The second and third IP's (in Koopmans' approximation) are then separated by about 0.6 eV. Employing, however, the more recent geometry of Bak and Skaarup [16] one finds that the two values are nearly identical having a separation of only 0.08 eV. In the many-body calculation the values of these two IP's remain nearly equal to each other in second order. In third order there is a reversal which is maintained in the calculation involving the renormalization procedure. But the splitting of the IP's is only 0.1 eV compared to about 0.8 eV from experiment. The assignment of the PES is thus uncertain. The calculation involving the larger s -, p -basis set was performed to see whether significant changes in the orbital energies arise. It was found that only very small changes in their values occurred for the outer valence orbitals. Consequently the double-zeta basis was enlarged with d -type polarization functions and the many-body calculations repeated. The basis set was not completely exhausted. The 29 virtual orbitals of lowest orbital energy were included in the calculation. The results of this calculation are listed in Table 4 and plotted together with the spectrum of Turner *et al.* [1] in Fig. 3. The first IP is the $6a'$ IP. The next one is the $5a'$ IP followed by the $3a''$ IP in contrast to the assignment of Basch *et al.* [2]. The separation between these IP's is 0.23 eV in third order and 0.17 eV in the

Table 4. Final results for the vertical valence IP's of ethylene imine (in eV)

| Symmetry | $-\epsilon_i^{SCF}$ | IP(2) | IP(3) | IP(R) | $P(R)$ | IP (exp) |
|----------|---------------------|--------------------|--------------------|--------------------|--------|----------|
| $6a'$ | 10.76 | 8.55 | 9.99 | 9.68 | 0.92 | 9.8 |
| $5a'$ | 13.09 | 11.30 | 12.28 | 12.05 | 0.92 | 11.8 |
| $3a''$ | 13.03 | 11.26 | 12.51 | 12.22 | 0.92 | 12.6 |
| $2a''$ | 14.48 | 12.96 | 13.46 | 13.37 | 0.93 | 13.6 |
| $4a'$ | 17.37 | 15.26 | 16.21 | 15.87 | 0.91 | 16.0 |
| $3a'$ | 19.05 | 16.85 | 17.83 | 17.49 | 0.90 | 17.5 |
| $1a''$ | 22.74 | 20.12 ^a | 20.78 ^a | 20.57 ^a | 0.88 | - |
| $2a'$ | 24.23 | 21.07 ^a | 22.16 ^a | 21.82 ^a | 0.87 | - |

^a These values cannot be very accurate as satellite lines are expected in this energy range (see text).

final result compared to the larger separation of about 0.8 eV from experiment. It was, however, found that enlargement of the orbital basis increased the separation and improved the agreement with experiment. The ordering of the remaining IP's agrees with the original assignment of Basch *et al.* The last two IP's ($1a''$ and $2a'$) have not been measured so far. The same comment as to the reliability of their values applies as made in the case of ethylene oxide. The agreement with experiment is satisfactory again, although the error for the $3a''$ IP, 0.38 eV, is larger than in the other cases, probably because the basis set was not completely exhausted.

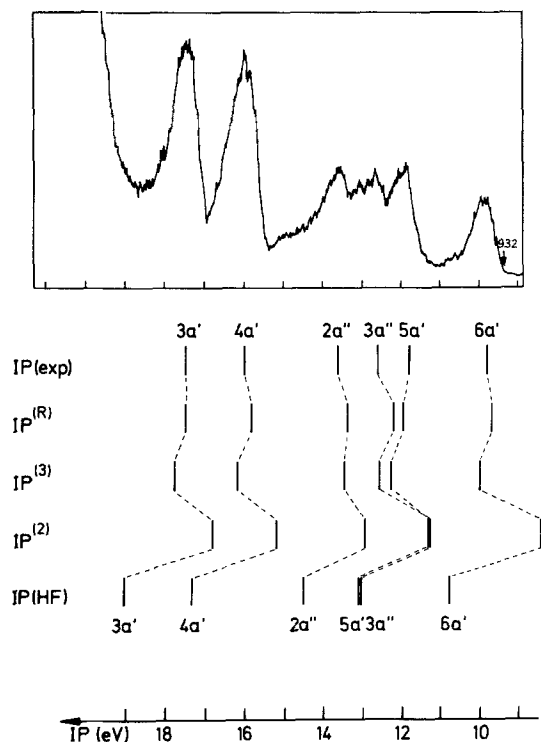


Fig. 3. Photoelectron spectrum of ethylene imine from Ref. [1] and calculated ionization potentials in different orders of the perturbation expansion

3. Conclusions

The vertical valence IP's of cyclopropane, ethylene oxide and ethylene imine are calculated by a many-body method. The basis sets employed are of double-zeta quality, sometimes supplemented by polarization functions (ethylene oxide and ethylene imine). In the case of cyclopropane it is confirmed that the original assignment of Basch *et al.* is correct concerning the ordering of the $2a'_1(\sigma)$ and $1a''_2(\pi)$ IP's. The $2a'_1$ IP is found to be smaller. Koopmans' theorem supplied the correct ordering of states: $2e'(\sigma)$, $1e''(\pi)$, $2a'_1(\sigma)$, $1a''_2(\pi)$, $1e'(\sigma)$. For ethylene oxide and ethylene imine Koopmans' theorem does not appear to supply the correct ordering. For ethylene oxide the two IP's in the third band system and for ethylene imine the second and third band have to be reassigned on the basis of the many-body calculations. The assignment of Basch *et al.* appears to be incorrect in these two cases. It must be mentioned, however, that in the case of ethylene imine the use of a more recent geometry is important for the understanding of the change of ordering. Some of the orbital energies are thus very sensitive to small geometry changes as might be expected for these strained small ring molecules. As the geometry used for ethylene oxide may be regarded as somewhat outdated it is still possible that a change of ordering might occur in the IP's whenever they are very close together as in the third band system. The ordering of the IP's of ethylene oxide is: $2b_1(\pi)$, $4a_1$, $1a_2(\pi)$, $2b_2$, $3a_1$, $1b_1(\pi)$, $1b_2$, $2a_1$, and for ethylene imine $6a'$, $5a'$, $3a''$, $2a''$, $4a'$, $3a'$, $1a''$, $2a'$. The agreement of the computed IP's with the experimental values is very satisfactory in general. The IP's at higher energy which have not been measured yet in the case of C_2H_4O and C_2H_5N will have larger errors if satellite lines are lying in their energy range, because the renormalization method as employed in this work is not justified then and the more general method of Ref. [19] should be used.

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