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SCF MO CI Perturbation Calculations of Inner Shell and Valence Shell Vertical Ionization Potentials

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A CI method for calculating inner and valence shell vertical ionization potentials is presented. It is based on *ab initio* SCF MO calculations for the neutral closed-shell ground state followed by CI perturbation calculations for the ground and ion states including all spin and symmetry adapted singly and doubly excited configurations with respect to the main configurations of the state of interest. The state energy is computed by performing a CI calculation for a set of selected configurations, and then adding the contributions of the remaining configurations as estimated by second order Brillouin–Wigner perturbation theory. The use of the same set of MO's for all states together with the CI perturbation method makes the method rather rapid. The numerical results are, in spite of the limited Gaussian basis sets used, in good agreement with experiment.

Key words: Configuration functions for CI, selection of ~ – Brillouin–Wigner perturbation theory – Calculation of vertical ionization potentials, *ab initio* ~

1. Introduction

Improvement over Koopmans' theorem [1] predictions of vertical ionization potentials (VIP's) requires a simultaneous calculation of the reorganization and correlation energies for neutral molecules and ions [2, 3]. This problem can be tackled both by configuration interaction (CI) methods and various variants of many-body perturbation theory [4–10].

Most of the CI variants described [11–14] so far are based on orbitals obtained for the ion state of interest (ordinarily from restricted open-shell SCF calculations) and include singly or higher excited configurations. Other workers [3, 15–18] make use of closed-shell SCF orbitals and build up ion doublet configurations (amongst them the Koopmans' configurations [19]) from this orbital basis set. These sorts of

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calculations have been restricted with respect to the types of configurations used (single excitation CI [16]) or their number taken account of [15]. Some authors use the Rayleigh–Schrödinger (RS) perturbation theory with the configurations as zeroth order wavefunctions up to the second [17] or third order [3] to obtain approximate VIP's. In our preceding CI work we considered single and limited sets of double excitations for the ground and cation states [18].

In the present paper we present a more general CI method based on molecular SCF orbitals (MO's) and usage of all spin and symmetry adapted singly and doubly excited configurations with respect to the state of interest (see below). To make the problem tractable or to save computer time the most important configurations are selected for an explicit CI treatment whilst the effects of the remaining configurations are estimated from a second order Brillouin–Wigner (BW) perturbation calculation [20].

2. Method

At first a brief outline of the method used to compute the energy E_ϕ of a state $|\phi\rangle$ is given. The method is valid for states of arbitrary charge and multiplicity.

Starting from a finite orthonormalized basis set of MO's $\{|\psi\rangle\}$ the finite orthonormalized basis set $\{|K\rangle\}$ of all possible configurations is generated. The use of spin and symmetry adapted configurations allows factoring the CI matrix and avoids complications [21] in handling configurations involving spin permutations among the same orbitals. In spite of spin and symmetry blocking, the CI problem thus defined is generally intractable because of its size and therefore needs simplification. As a first step in this direction a set of main configurations (MC's) [22] $\{|M\rangle\}$ is specified. It includes the most important configurations.

All configurations differing from the MC's by higher than double excitations are neglected. They are referred to as the set of neglected configurations (NC's) $\{|N\rangle\}$. From all other configurations a set of selected configurations (SC's), $\{|S\rangle\}$ is singled out according to their strength of interaction with the MC's. The set of remaining configurations (RC's) $\{|R\rangle\}$ is supposed to influence E_ϕ only due to their huge number. Thus the configurational space is divided into the four subspaces $\mathbb{M}$, $\mathbb{S}$, $\mathbb{R}$, and $\mathbb{N}$ spanned by the subsets $\{|M\rangle\}$, $\{|S\rangle\}$, $\{|R\rangle\}$, and $\{|N\rangle\}$.

The search for the SC's is accomplished by the following selection procedure First the MC's CI matrix H_M with elements $\langle M|\boldsymbol{H}|M'\rangle$ ($\boldsymbol{H}$ being the non-relativistic Hamiltonian of the system under study) is constructed and diagonalized. The resulting set of eigenvectors $\{|M_v\rangle\}$ with

$$|M_v\rangle = \sum_M C_{MM_v}|M\rangle \tag{1}$$

is thereafter referred to as the set of selection vectors (SV's). A configuration $|K\rangle$ neither belonging to $\mathbb{M}$ nor $\mathbb{N}$ is selected: 1) if its contribution $|\Delta E_{M_v}|$ to the second-order RS perturbation energy from its interaction with one of the SV's is larger than or equal to a theshold value T, i.e.

$$|\Delta E_{M_v}|=|\langle M_v|\boldsymbol{H}|K\rangle|^2/|E_{M_v}-E_K|\geqslant T \tag{2}$$

or 2) if it is lower in energy than one of the SV's by less than a specified amount G, i.e.

$$0<(E_{M_v}-E_K)<G \tag{3}$$

Degenerate configurations are incorporated into $\mathbb{S}$ if at least one of them meets (2) and (3). Note that (2) assures selection of the configurations mostly contributing to the state function $|\phi\rangle$ and (3) avoids difficulties with the subsequent perturbation procedure.

CI selection procedures have been known for a long time [23, 24] and have been widely used [21, 22, 25]. Most of them are based on second-order RS perturbation theory [21, 23–25] and in one case [22] small test matrices are diagonalized Some others [21, 25] are iterative procedures. For the present work the selection procedure chosen is not considered a critical point because of subsequent perturbative corrections.

After the subset $\{|S\rangle\}$ being determined there is no longer any need to differentiate between the $\{|M\rangle\}$ and $\{|S\rangle\}$ sets and henceforth $\{|M\rangle\}$ is considered a part of $\{|S\rangle\}$. Then the matrix H_S with elements $\langle S|\boldsymbol{H}|S'\rangle$ is set up. Its diagonalization yields the zeroth order approximations

$$|\phi^{(0)}\rangle=\sum_S C_{S\phi}{}^{(0)}|S\rangle \tag{4}$$

and $E_\phi^{(0)}$ for $|\phi\rangle$ and E_ϕ, respectively.

To define the perturbation operator $\boldsymbol{H}'$ we cannot start from the exact (as defined above) Hamiltonian $\boldsymbol{H}$ as

$$\boldsymbol{H}=\boldsymbol{F}+\boldsymbol{V} \tag{8}$$

where $\boldsymbol{F}$ is the Hartree–Fock (HF) operator and $\boldsymbol{V}$ is known as the "fluctuation potential" [26] but instead must resort to the approximate Hamiltonian $\tilde{\boldsymbol{H}}$ written as

$$\tilde{\boldsymbol{H}}=\boldsymbol{F}+\tilde{\boldsymbol{V}} \tag{9}$$

with

$$\tilde{\boldsymbol{V}}=\boldsymbol{V}-\sum_N\sum_{N'}\boldsymbol{O}_N\boldsymbol{V}\boldsymbol{O}_{N'} \tag{10}$$

where $\boldsymbol{O}_K$ is the configurational projection operator

$$\boldsymbol{O}_K=|K\rangle\langle K| \tag{11}$$

and the sums in (10) extend over all configurations in $\mathbb{N}$. Thus using (10) instead of $\boldsymbol{V}$ is equivalent of neglecting all configurations in $\mathbb{N}$. Since, however $\tilde{\boldsymbol{V}}$ is still too large to be considered as perturbation we define the unperturbed Hamiltonian $\boldsymbol{H}_0$

and the perturbation operator $\boldsymbol{H}'$ through

$$\tilde{\boldsymbol{H}}=\boldsymbol{H}_0+\boldsymbol{H}' \tag{12}$$

with

$$\boldsymbol{H}_0=\boldsymbol{F}+\boldsymbol{V}_0 \tag{13}$$

$$\boldsymbol{H}'=\tilde{\boldsymbol{V}}-\boldsymbol{V}_0 \tag{14}$$

and

$$\boldsymbol{V}_0=\sum_{S}\sum_{S'}\boldsymbol{O}_S\boldsymbol{V}\boldsymbol{O}_{S'}+\sum_{R}\sum_{R'}\boldsymbol{O}_R\boldsymbol{V}\boldsymbol{O}_{R'}\cdot\delta_{E_R E_{R'}} \tag{15}$$

where the first double sum in (15) extends over all configurations in $\mathbb{S}$ and the second one over those in $\mathbb{R}$. Thus the first term accounts for the configurations in $\mathbb{S}$ space and the second term for the diagonal and degenerate ones in $\mathbb{R}$ space.

Partitioning of $\tilde{\boldsymbol{H}}$ according to (12) to (15) means that the functions $|\phi^{(0)}\rangle$ and energies $E_\phi^{(0)}$ are eigenfunctions and eigenvalues of $\boldsymbol{H}_0$ in $\mathbb{S}$ space. In $\mathbb{R}$ space non-degenerate RC's are eigenfunctions of $\boldsymbol{H}_0$ with eigenvalues $E_R=\langle R|\boldsymbol{H}|R\rangle$ and some degenerate subset $\{|R_d\rangle\}$ has eigenfunctions

$$|R_v\rangle=\sum_{R_d}C_{R_dR_v}|R_d\rangle \tag{16}$$

with eigenvalues $E_{R_v}=\langle R_v|\boldsymbol{H}|R_v\rangle$ obtained by diagonalizing the submatrix H_{R_d}. To simplify the notation we henceforth use $\{|R^{(0)}\rangle\}$ for all eigenfunctions of $\boldsymbol{H}_0$ in $\mathbb{R}$ space. Accordingly $\boldsymbol{H}'$ has no diagonal elements (i.e. no first order corrections) and only vanishing matrix elements in $\mathbb{S}$ space but couples all configurations of $\mathbb{S}$ space with those of $\mathbb{R}$ space and the configurations of $\mathbb{R}$ space with themselves.

The effects of the $\mathbb{R}$-space configurations on the wavefunctions $|\phi^{(0)}\rangle$ are approximately taken account of by second-order BW perturbation theory according to the formula.

$$E_\phi^{(2)}=E_\phi^{(0)}+\sum_{R^{(0)}}|\langle\phi^{(0)}|\boldsymbol{H}'|R^{(0)}\rangle|^2/(E_\phi^{(2)}-E_R^{(0)}). \tag{17}$$

(17) must be solved iteratively. Only a few iterations are sufficient to calculate $E_\phi^{(2)}$ to an accuracy of 10^{-8} a.u. The final BW corrected state function then is

$$|\phi^{(1)}\rangle=N(|\phi^{(0)}\rangle+\sum_{R^{(0)}}C_{R^{(0)}\phi^{(1)}}|R^{(0)}\rangle) \tag{18}$$

with

$$c_{R^{(0)}\phi^{(1)}}=\langle\phi^{(0)}|H'|R^{(0)}\rangle/(E_\phi^{(2)}-E_R^{(0)}) \tag{19}$$

and

$$N=(1+\sum_{R^{(0)}}|c_{R^{(0)}\phi^{(1)}}|^2)^{-1/2}. \tag{20}$$

Application of RS perturbation theory yields less satisfactory results. It overestimates the energy gain for the lower roots as a consequence of its non-iterative nature [20].

Note that the BW calculation is equivalent to the diagonalization of a matrix which just contains all matrix elements involved in the perturbation formula (17).

CI perturbation methods with CI vectors as zeroth order approximations have been previously used [25, 27]. The methods differ however, in treating the degenerate RC's and additionally either in using inferior [20] RS instead of BW theory [25] or in disregarding configurational selection procedures [27].

3. Application of the Method to the Calculation of Vertical Ionization Potentials

The vertical ionization potentials (VIP's) are calculated as the difference in energy between the various ion states and the molecular ground state. The state energies are obtained by applying the CI method of the previous section. All types of single and double excitations are considered. Besides the Koopmans' configuration A we have two sorts of single excitations B and C and four types of double excitations D, E, F, and G. Occupations corresponding to C, E, F (three unpaired electrons, three determinants) lead to two different doublet configurations [28]. For G (five unpaired electrons, ten determinants), we have five doublet configurations with coefficients obtained by the Clebsch–Gordan formalism [29]. All matrix elements have been obtained with a computer program that is based on the explicit expressions for the different matrix elements. This program has been widely checked against a general brute force matrix element program. All molecular orbitals (MO's) generated in the closed shell SCF procedure have been considered.

The selection parameters (cf. the previous section) have been chosen as follows. The gap parameter G was set equal to 0.5 a.u. (i.e. 13.605 eV) and kept fixed for all calculations performed. The threshold parameter T varied between 0.01 and 0.02 eV. Accordingly, the space $\mathbb{S}$ was spanned by 90 to 150 symmetry-adapted SC's in the actual calculations. The total number of configurations was up to several thousands. The same T value was used for all states of a given molecule. The various total energies reached for the molecules studied in this paper are summarized in Table 1. Here E_{SCF}, E_{CI} and E_{PERTCI} are the SCF, the $\mathbb{S}$-space CI and the CI plus BW perturbational results. It is very important that E_{PERTCI} and particularly the VIP's based on the molecular PERTCI calculations are rather

Table 1. Total energies without and with CI

Molecule	T (eV)	E_{SCF} (a.u.)	E_{CI} (a.u.)	E_{PERTCI} (a.u.)
H_2O	0.01	−75.907390	−76.030229	−76.037937
N_2	0.015	−108.815623	−109.006778	−109.042925
C_2H_2	0.02	−76.720501	−76.869881	−76.932564
CH_2O	0.02	−113.681759	−113.816763	−113.894016
CO	0.02	−112.552355	−112.716555	−112.751251

stable with changes in T meaning that the particular value of T chosen is not a critical point. These findings are demonstrated for N_2 in Figs. 1 and 2, respectively.

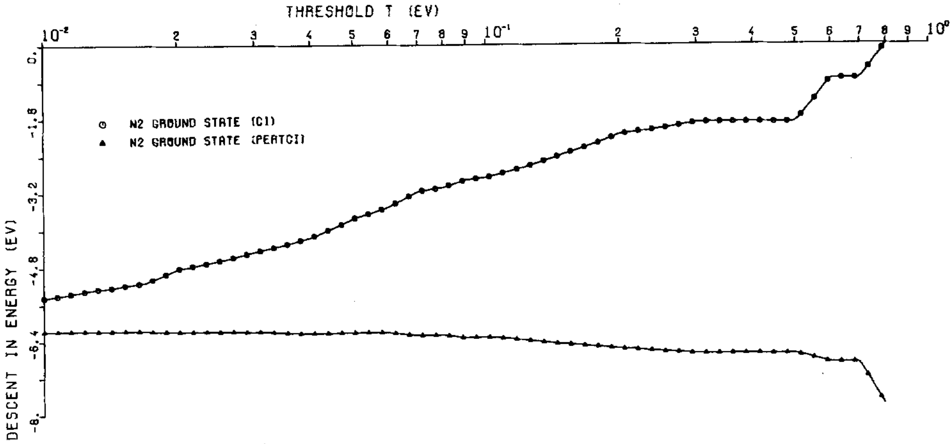

Fig. 1. CI and PERTCI descents in total ground state energy of N_2 (i.e.: CI and PERTCI minus SCF ground state energies) vs. thresholds T

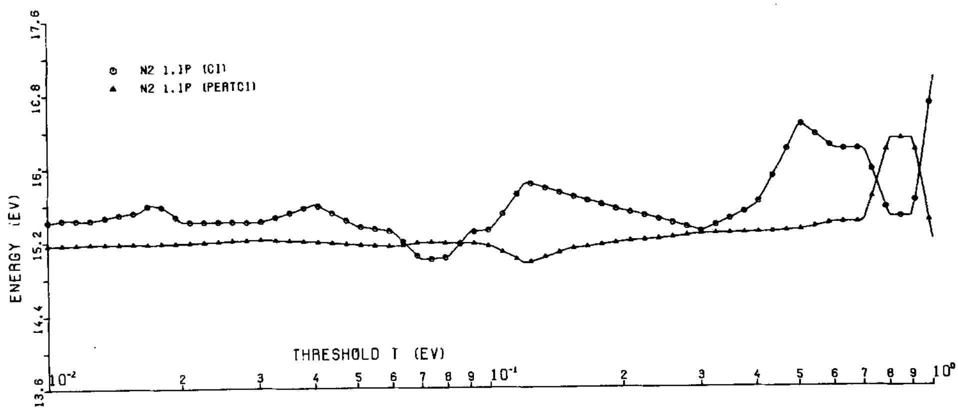

Fig. 2. CI and PERTCI first VIP of N_2 vs. thresholds T

For most calculations one MC proved to be sufficient, namely the closed shell ground state configuration on one hand and the Koopmans' configurations for the ion states on the other. Exceptions to this rule pertain to the second $^2B_2$ state of CH_2O where two MC's have been used with the selection criterions (Eqs. (2) and (3)) being applied to one of the resulting SV's (henceforth abbreviated as 2M1S), the third $^2A_1$ state of the same molecule and third $^2\Sigma^+$ of CO where selections of 3M3S and 3M1S types respectively have been applied. For a more detailed discussion of these cases see the next section.

All calculations of the present paper have been done using 4-31 G basis sets [33] and experimental geometries [30–32]. For N_2 and C_2H_2 one s and two p_π type bond polarization (BP) functions have been placed midway between the heavy atoms. The exponents of the NN BP functions have been optimized ($\alpha_S = 1.7$, $\alpha_p = 0.8$). The corresponding CC exponents are taken from literature [34]. The SCF calculations were performed with the POLYATOM program system [35].

The computational efforts of the method are rather moderate. The CPU time used to compute one VIP is of the same order as for one SCF calculation when all occupied and virtual MO's are included. The most time consuming step is the transformation of repulsion integrals from the AO to the MO basis. It has to be done however only once for all states of a molecule.

4. Results and Discussion

Our calculated VIP's ($-\varepsilon$ = Koopmans' IP's, IP_{CI}'s = $\mathbb{S}$-space CI, IP_{PERTCI}'s = CI plus BW perturbational treatment) are gathered for H_2O, N_2, C_2H_2, CH_2O and CO in Tables 2–6, respectively along with the experimental values and various sets of otherwise obtained theoretical data. In view of the 4-31 G basis set used the results are surprisingly good. The PERTCI results are generally only slightly better than the CI ones indicating that the Koopmans' defects are predominantly accounted for by the SC's and that the contributions of the RC's to the state energies, though not small, generally cancel when the difference of the state energies are taken. However exceptions do occur so that PERTCI calculations must be always carried out (cf. e.g. the $1b_1$ ionization of CH_2O).

Our VIP's tend to be a bit too low for the lower ionization and bit too high for the higher ionizations. We presume that these minor defects are due to the rather limited basis set used. It is well known in literature [9, 40] that CI and perturbational results are rather basis set dependent So it is to be expected that Koopmans' defects cannot be assumed to be basis set independent. A rather drastic example for that is already contained in literature [38, 41, 47] for N_2 and CH_2O (cf. the $IP_{MB\text{-}GF}$'s of Tables 3 and 5 of the present paper).

In some cases difficulties may arise in assigning VIP's to MO's. In most cases the Koopmans' configuration contributes 80% and more to the computed wavefunction and the assignment is unambiguous. Sometimes, however, there is strong mixing of the Koopmans' configuration with other configurations (usually higher excited "shake up" configurations and sometimes even another Koopmans' configuration), and the contribution of the Koopmans' configuration may become less than 50%. In such cases the same Koopmans' configuration is contained with large coefficients in more than one wavefunction. In these cases we have assigned the states with respect to the configurations with the largest expansion coefficient and marked this by an asterisk (*) in the tables.

In such strong mixing cases pure perturbational expansions may fail to converge [40]. Examples are the $3a_1$ ionization of CH_2O (cf. the RSPT results of Table 5) and the $3\sigma^+$ ionization of CO (cf. the RSPT results of Table 6). Here CI treatments are unavoidable. Finally it should be noted that our calculations predict several

Table 2. Vertical IP's of H_2O

MO	$-\varepsilon$ (eV)	$\mathrm{IP}_{\mathrm{CI}}$ (eV)	$\mathrm{IP}_{\mathrm{PERTCI}}$ (eV)	$\mathrm{IP}_{\mathrm{EXP}}{}^{a}$ (eV)	$\mathrm{IP}_{\mathrm{MB\text{-}GF}}{}^{b}$ (eV)	$\mathrm{IP}_{\Delta\mathrm{CEPA}}{}^{c}$ (eV)	$\mathrm{IP}_{\mathrm{QD\text{-}MBPT}}{}^{d}$ (eV)	$\mathrm{IP}_{\mathrm{RSPT}}{}^{e}$ (eV)
$1a_1$	558.33	542.08	541.94	539.7	—	539.60	—	538.44
$2a_1$	36.80	33.72	32.74	32.2	34.82	32.34	35.19	32.02
$1b_2$	19.25	19.02	18.86	18.55 (18.72)	18.96	18.85	19.24	18.72
$3a_1$	15.19	14.20	14.04	14.73 (14.83)	14.91	14.68	14.73	13.93
$1b_1$	13.59	12.18	12.03	12.61 (12.78)	12.69	12.48	12.73	12.06

[a] Refs. [36, 37, 14], values in brackets are corrected [14].

[b] Ref. [38]; MB-GF: Many Body Green's Function results; contracted Gaussian basis: O (*9s5p1d/4s2p1d*), H (*4s1p/2s1p*).

[c] Ref. [14]; Gaussian basis: O (*11s, 7p, 4d, 1f*), H (*5s1p*), *1s* for every bond.

[d] Ref. [39]; QD-MBPT: Quasi Degenerate Many Body Perturbation Theory; contracted Gaussian basis: O (*10s6p/5s3p*), H (*4s/2s*) augmented by a set of oscillator orbitals.

[e] Ref. [40]; RSPT: Rayleigh-Schrödinger Perturbation Theory; double zeta STO basis.

Table 3. Vertical IP's of N_2

MO	$-\varepsilon$ (eV)	$\mathrm{IP}_{\mathrm{CI}}$ (eV)	$\mathrm{IP}_{\mathrm{PERTCI}}$ (eV)	$\mathrm{IP}_{\mathrm{EXP}}{}^{a}$ (eV)	$\mathrm{IP}_{\mathrm{MB\text{-}GF}}{}^{b}$ (eV)	$\mathrm{IP}_{\mathrm{SDSBC}}{}^{c}$ (eV)	$\mathrm{IP}_{\mathrm{EOM}}{}^{d}$ (eV)	$\mathrm{IP}_{\mathrm{RSPT}}{}^{e}$ (eV)
$1\sigma_g$	426.19	414.85	414.83	409.9	—	410.80	—	—
$1\sigma_u$	426.29	414.91	414.93		—	410.72	—	—
$2\sigma_g$	40.57	40.17	40.17	37.3	—	37.92	—	—
$2\sigma_u$	20.68	18.81	18.49	18.78	19.01; 18.43	17.55	18.63	18.39
$1\pi_u$	16.82	17.03	16.73	16.98	16.80; 16.43	17.23	17.03	16.67
$3\sigma_g$	16.96	15.51	15.18	15.60	15.31; 14.95	14.91	15.69	14.90

[a] Refs. [36, 37].

[b] Ref. [41]; contracted Gaussian basis: N (*11s7p1d/5s4p1d*) for the first values and N (*9s5p/4s2p*) for the second values.

[c] Ref. [9]; SDSBC: Symmetry Diagonalized Shifted Born Collision; double zeta STO basis for $2p_\sigma$, $2p_\pi$ and single zeta STO basis for *1s*, *2s*, $3d_\sigma$, $3d_\pi$.

[d] Ref. [42]; EOM: Equation of Motion Technique; double zeta STO basis for *1s*, *2s*, *2p* and single zeta STO basis for *3d*.

[e] Ref. [43]; contracted Gaussian basis: N (*9s5p/4s2p*).

Table 4. Vertical IP's of C_2H_2

MO	$-\varepsilon$ (eV)	$\mathrm{IP_{CI}}$ (eV)	$\mathrm{IP_{PERTCI}}$ (eV)	$\mathrm{IP_{EXP}}^a$ (eV)	$\mathrm{IP_{MB\text{-}GF}}^b$ (eV)
$1\sigma_g$	305.21	295.29	295.89	291.14	—
$1\sigma_u$	305.11	295.26	295.62		
$2\sigma_g$	27.60	25.04	25.02	23.33	26.05
$2\sigma_u$	20.55	19.57	19.26	18.75	18.89
$3\sigma_g$	18.17	17.45	17.11	16.72	16.98
$1\pi_u$	10.75	11.32	10.90	11.40	11.06

[a] Refs. [37, 44].

[b] Ref. [38], contracted Gaussian basis: C (9*s*5*p*/4*s*2*p*), H (4*s*/2*s*).

Table 5. Vertical IP's of CH_2O

MO	$-\varepsilon$ (eV)	$\mathrm{IP_{CI}}$ (eV)	$\mathrm{IP_{PERTCI}}$ (eV)	$\mathrm{IP_{EXP}}^a$ (eV)	$\mathrm{IP_{MB\text{-}GF}}^b$ (eV)	$\mathrm{IP_{MB\text{-}GF}}^c$ (eV)	$\mathrm{IP_{RSPT}}^d$ (eV)
$1a_1$	559.19	542.44	542.74	539.4	—	—	540.23
$2a_1$	307.69	297.30	297.21	294.5	—	—	293.38
$3a_1$	38.64	37.37*	36.81*	—	—	—	—
$4a_1$	24.80	23.36	22.50	21.8	—	—	21.87
$1b_2$	19.63	18.42*	17.86*	16.78	17.86	17.13	17.59
$5a_1$	17.57	16.06	16.02	16.00	16.26	16.36	16.19
$1b_1(\pi)$	14.36	14.72	14.37	14.38	14.35	14.29	14.73
$2b_2$	12.16	10.99	10.62	10.88	10.92	10.84	11.15

[a] Refs. [37, 45, 46].

[b] Ref. [38]; contracted Gaussian lobe basis: C, O (11*s*6*p*/5*s*3*p*); H (5*s*/1*s*).

[c] Ref. [47]; contracted Gaussian basis: C, O (11*s*7*p*1*d*/7*s*5*p*1*d*), H (6*s*1*p*/4*s*1*p*).

[d] Ref. [40]; double zeta STO basis.

Table 6. Vertical IP's of CO

MO	$-\varepsilon$ (eV)	$\mathrm{IP_{CI}}$ (eV)	$\mathrm{IP_{PERTCI}}$ (eV)	$\mathrm{IP_{EXP}}^a$ (eV)	$\mathrm{IP_{RSPT}}^b$ (eV)	$\mathrm{IP_{MB\text{-}GF}}^c$ (eV)
$1\sigma^+$	561.76	545.94	545.82	542.1	545.01	540.73
$2\sigma^+$	309.33	300.19	299.79	295.9	296.97	298.68
$3\sigma^+$	42.37	40.84*	38.51*	38.3	—	
$4\sigma^+$	21.61	19.95	19.56	19.72	20.51	
1π	17.41	17.28	16.87	16.91	18.02	
$5\sigma^+$	14.93	13.64	13.19	14.01	14.08	

[a] Refs. [48, 37].

[b] Ref. [40]; single zeta STO basis for 1*s*, double zeta STO basis for 2*s*, 2*p*.

[c] Ref. [49]; contracted Gaussian basis.

shake-up transitions in the region of 20–40 eV which are not shown in the tables and which have not yet been identified in the spectra Even the $3a_1$ ionization of CH_2O that may be described as Koopmans' transition with a very large shake-up admixture has not been experimentally characterized.

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