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# Benchmark calculations of K-edge ionization energies for first-row elements using scalar-relativistic core-valence-separated equation-of-motion coupled-cluster methods

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37  
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39 **Abstract**

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Benchmark scalar-relativistic core-valence-separated (CVS) equation-of-motion coupled-cluster ionization potential (EOMIP-CC) calculations of 21 K-edge ionization energies of C, O, N, and F in 14 molecules are reported. The CVS-EOMIP-CC methods are shown to be numerically more stable and more accurate than the parent EOMIP-CC methods, even when the calculations using the latter can be tightly converged. The superior performance of the CVS scheme is attributed to the exclusion of spurious couplings between core-ionized states and valence continuum states. Systematic improvement of computed K-edge ionization energies within the CVS-EOMIP-CC hierarchy, including the CC singles and doubles (CCSD) method, the CC singles, doubles and

triples (CCSDT) method, and the CC singles, doubles, triples, and quadruples (CCSDTQ) method, is demonstrated, with CCSDTQ yielding essentially quantitative results. Maximum absolute deviations between computed and experimental results amount to 2.54 eV for CCSD/cc-pCVQZ, 0.54 eV for CCSDT/cc-pCVQZ, and 0.23 eV for CCSDT/cc-pCVQZ augmented with quadruples contributions using the cc-pVTZ basis sets. The corresponding standard deviations are 1.91 eV for CCSD/cc-pCVQZ, 0.18 eV for CCSDT/cc-pCVQZ, and 0.10 eV for CCSDT/cc-pCVQZ augmented with quadruples contributions using the cc-pVTZ basis sets. Finally, CVS-EOMIP-CCSDT/cc-pCVTZ calculations of core ionization energies in  $\text{CH}_3\text{CN}$  and  $\text{CH}_3\text{NC}$  are reported, and experimental re-investigation of carbon 1s ionization energies in  $\text{CH}_3\text{CN}$  is suggested.

## 1 Introduction

X-ray spectroscopy is widely used for probing electronic structure and dynamics in molecules, solid state, and biological systems.<sup>1-4</sup> In particular, recent advancements in short-pulse X-ray light sources including synchrotrons, free-electron lasers, and those based on high-harmonic generation<sup>5-11</sup> have enabled the study of ultrafast nuclear and electronic dynamics.<sup>12-17</sup> Extensive studies of computational techniques aiming at accurate calculations of X-ray photoelectron and absorption spectra are available in the literature.<sup>18,19</sup> The computational techniques can be classified into two broad categories. The ones in the first category perform separate orbital optimizations for core-ionized or excited states. The delta-Hartree-Fock ( $\Delta\text{HF}$ ) method,<sup>20-23</sup> the delta-density-functional-theory ( $\Delta\text{DFT}$ ) method<sup>23,24</sup> as well as its approximate variants,<sup>24-27</sup> the delta-restricted-active-space self-consistent-field ( $\Delta\text{RASSCF}$ ) method,<sup>21,28-30</sup> the orthogonality-constrained DFT method,<sup>31</sup> the static exchange (STEX) method,<sup>32,33</sup> and the non-orthogonal configuration interaction singles (NOCIS) method<sup>34</sup> fall into this category. These techniques explicitly account for the strong orbital relaxation induced by the creation of core hole(s) and are usually capable of providing good energies

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3 for core-ionized/excited states. Calculations with explicit inclusion of dynamical correlation  
4 on top of  $\Delta\text{HF}$  have also been reported.<sup>35–38</sup> The techniques in the second category use the  
5 ground state of the neutral molecule as the reference state and access core-ionized and excited  
6 states via response theory or using a wave operator that accounts for the difference between  
7 ground and excited states. The configuration interaction singles (CIS) method,<sup>39–41</sup> CIS  
8 with perturbative inclusion of double excitations (CIS(D)),<sup>42</sup> time-dependent DFT linear re-  
9 sponse (TDDFT-LR) theory,<sup>18,43</sup> the Bethe-Salpeter equation approach,<sup>44</sup> Green’s function  
10 methods,<sup>45–48</sup> equation-of-motion coupled-cluster (EOM-CC) methods<sup>49,50</sup>/coupled-cluster  
11 linear response (CC-LR) theory<sup>51,52</sup> and multireference coupled-cluster methods<sup>53–56</sup> belong  
12 to this category. We mention that real-time DFT<sup>57–59</sup> and CC methods<sup>60</sup> for calculations  
13 of core-ionized/excited states fall into the second category within the present discussion, as  
14 the ionization or excitation energies computed with these methods are identical to those  
15 obtained using the corresponding linear response theories.  
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29 Response theories (and the methods in the second category in general) are flexible tools  
30 for calculations of both energies and properties of excited states. However, additional chal-  
31 lenges have to be dealt with in calculations of core-ionized or excited states. Since core-  
32 ionized and excited states are energetically embedded in continuum states, the convergence of  
33 excited-state equations has emerged as a major challenge. Several schemes including the com-  
34 plex polarization propagator (CPP) method,<sup>61</sup> the (asymmetric) Lanczos algorithm,<sup>62</sup> the  
35 Arnoldi algorithm,<sup>49</sup> the energy-specific strategy,<sup>50</sup> and the core-valence separation (CVS)  
36 scheme<sup>52,63</sup> have been proposed in order to resolve the convergence difficulty. Among these  
37 approaches, the CVS scheme originally proposed by Cederbaum et al.<sup>64</sup> appears to be the  
38 most promising. The CVS scheme retains only excitations involving at least one core orbitals  
39 and thus excludes the problematic pure valence excitations that are (quasi-)degenerate to the  
40 core-ionized or excited states of interest. In the literature the CVS scheme has been referred  
41 to as “the CVS approximation” to the parent “full” method. However, the “full method” may  
42 include spurious couplings between core-ionized or excited states and valence continuum  
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3 states. One motivation of the present study is to examine the numerical significance of this  
4 problem of the “full” method. It has indeed been found and will be reported in Section 3.1  
5 that the CVS scheme is superior to the “full” method and thus is the method of choice for  
6 treating core-ionized and excited states.  
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11 On the other hand, the solution of response equations within the CVS scheme does  
12 neglect the contribution from the continuum part of the wave function of core-ionized or  
13 excited states. This is a potential source of errors for the computed energies and properties  
14 of core-ionized or excited states. Another motivation of this work is to investigate the in-  
15 trinsic accuracy of this approximation. For this purpose, the hierarchy of CVS-EOMIP-CC  
16 methods,<sup>65–69</sup> including the CC singles and doubles (CCSD) method,<sup>66</sup> the CC singles, dou-  
17 bles and triples (CCSDT) method<sup>70,71</sup> as well as CC singles, doubles, triples, and quadruples  
18 (CCSDTQ) method,<sup>72</sup> together with correlation-consistent basis sets<sup>73–75</sup> have been used to  
19 systematically approach the exact solution for the bound part of the wave function. The  
20 benchmark set comprises 21 K-edge ionization energies of C, N, O, F in 14 molecules. Note  
21 that relativistic effects essentially contribute a constant shift of K-edge ionization energies in  
22 C, N, O, or F. However, relativistic corrections amount to about 0.1 eV for C and around 0.7  
23 eV for F. They are not negligible when high accuracy is desired.<sup>76,77</sup> In the present study we  
24 have used spin-free exact-two-component theory in its one-electron variant (SFX2C-1e)<sup>78,79</sup>  
25 to treat relativistic effects. Theory and computational details are given in Section 2, while  
26 the computational results are presented and discussed in Section 3. The conclusion is given  
27 in Section 4.  
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## 47 Theory and computational details

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49 We first briefly recapitulate the equation-of-motion ionization-potential coupled-cluster (EOMIP-  
50 CC) methods<sup>80</sup> used in the present study. Throughout the discussion, we follow the standard  
51 convention that  $\{i, j, \dots\}$ ,  $\{a, b, \dots\}$ , and  $\{p, q, \dots\}$  denote occupied, virtual, and arbitrary  
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orbitals, respectively. The EOMIP-CC wave function  $|\Psi^{\text{EOMIP-CC}}\rangle$  is obtained by applying an “ionization operator”  $\hat{R}$  to the ground state CC wave function  $|\Psi^{\text{CC}}\rangle$ , i.e.,

$$|\Psi^{\text{EOMIP-CC}}\rangle = \hat{R}|\Psi^{\text{CC}}\rangle. \quad (1)$$

The wave operator of the ground state CC method takes an exponential parametrization and the CC wave function can be written as  $|\Psi^{\text{CC}}\rangle = e^{\hat{T}}|0\rangle$ , in which  $|0\rangle$  is the reference determinant. The cluster operator  $\hat{T}$  is a weighted combination of excitation operators, e.g., in the CC singles and doubles (CCSD) method  $\hat{T} = \sum_{ia} t_i^a a_a^\dagger a_i + \frac{1}{4} \sum_{ijab} t_{ij}^{ab} a_a^\dagger a_b^\dagger a_j a_i$ . The cluster amplitudes are determined by projected amplitude equations

$$\langle \Phi^{\text{EX}} | \bar{H} | 0 \rangle = 0, \quad (2)$$

in which  $\bar{H}$  denotes the similarity-transformed Hamiltonian,  $\bar{H} = e^{-\hat{T}} \hat{H} e^{\hat{T}}$ , and  $\Phi^{\text{EX}}$  represents excited determinants generated by the elementary excitation operators in  $\hat{T}$ , e.g., in CCSD method  $\{|\Phi^{\text{EX}}\rangle\} = \{a_a^\dagger a_i | 0 \rangle\} \cup \{a_a^\dagger a_b^\dagger a_j a_i | 0 \rangle\}$ . The manifold of elementary ionization operators in  $\hat{R}$  is chosen to be consistent with the excitation manifold in  $\hat{T}$ . In the CCSD method, the ionization operator  $\hat{R}$  is a weighted combination of  $\{a_i\}$  and  $\{a_a^\dagger a_j a_i\}$ , i.e.,  $\hat{R} = \sum_i r_i a_i + \frac{1}{2} \sum_{ij,a} r_{ij}^a a_a^\dagger a_j a_i$ . The amplitudes  $r_i$  and  $r_{ij}^a$  are determined by configuration-interaction (CI)-like secular equations involving  $\bar{H}$

$$\langle \Phi^{\text{IP}} | [\bar{H}, \hat{R}] | 0 \rangle = E^{\text{IP}} \langle \Phi^{\text{IP}} | \hat{R} | 0 \rangle. \quad (3)$$

in which  $|\Phi^{\text{IP}}\rangle$ 's are ionized states generated by the same manifold of elementary ionization operators as in  $\hat{R}$ , e.g.,  $\{|\Phi^{\text{IP, CCSD}}\rangle\} = \{a_i | 0 \rangle\} \cup \{a_a^\dagger a_j a_i | 0 \rangle\}$ . In the EOMIP-CC calculations, the ground state equations [Eq. (2)] are first solved and then the secular equation [Eq. (3)] is solved for each ionization energy of interest. The present study has employed the series of CCSD, CCSDT, and CCSDTQ methods to systematically approach the full CI limit. The

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3 EOMIP-CCSDT method includes triple excitations  $\{a_a^\dagger a_b^\dagger a_c^\dagger a_k a_j a_i\}$  in  $\hat{T}$  and ionizations with  
4 two shake-up excitations  $\{a_a^\dagger a_b^\dagger a_k a_j a_i\}$  in  $\hat{R}$ , while the EOMIP-CCSDTQ method further  
5 includes quadruple excitations  $\{a_a^\dagger a_b^\dagger a_c^\dagger a_d^\dagger a_l a_k a_j a_i\}$  in  $\hat{T}$  and ionizations with three shake-  
6 up excitations  $\{a_a^\dagger a_b^\dagger a_c^\dagger a_l a_k a_j a_i\}$  in  $\hat{R}$ . As all the molecules studied here are closed-shell  
7 systems, the recent implementation of non-orthogonal spin adaptation for CCSDTQ and  
8 EOM-CCSDTQ methods<sup>81,82</sup> has played an essential role in the present calculations. We  
9 mention that all EOMIP-CCSDTQ calculations presented here have been carried out using  
10 the EOM-CCSDTQ code for excitation energies (EE) together with the “continuum-orbital  
11 trick”, i.e., the electron to be ionized is promoted into a “continuum” orbital with zero orbital  
12 energy and no coupling with other orbitals in order to obtain the ionized state.<sup>83</sup>

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23 The core-valence separation (CVS) scheme includes in  $\hat{R}$  only elementary ionization op-  
24 erators that contain at least one core orbital. A simple scheme for the implementation of  
25 CVS in a standard EOMIP-CC code suggested by Coriani and Koch has been used in the  
26 CVS-EOMIP-CCSD and CVS-EOMIP-CCSDT calculations presented here. Namely, all the  
27 R amplitudes for pure valence ionizations  $\{r_{i_v}\}$ ,  $\{r_{i_v j_v}^a\}$  and etc, in which  $\{i_v, j_v, \dots\}$  rep-  
28 represents occupied valence orbitals, are set to zero during the solution of EOMIP-CC secular  
29 equations. The CVS-EOMEE-CCSDTQ calculations using continuum-orbital trick presented  
30 here have been carried out using an efficient implementation of the CVS scheme, in which  
31 only the R amplitudes involving core orbitals are included in the calculation. The details  
32 about the efficient implementation of the CVS scheme for the EOM-CCSDT and EOM-  
33 CCSDTQ methods go beyond the present context and will be published elsewhere. It should  
34 be mentioned that the original proposal of CVS by Cederbaum et al. neglects Hamiltonian  
35 integrals that couple valence and core orbitals. This leads to the same scheme for the solution  
36 of excited-state secular equation adopted here together with the frozen-core approximation  
37 for the ground state calculation.<sup>84</sup> The purpose of the current study is to benchmark the  
38 performance of CVS-EOMIP-CC methods for calculations of core ionization energies. In par-  
39 ticular, we aim to understand how the results converge with respect to the excitation rank  
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3 and how the near-CVS-FCI limit compares with experiment. Therefore, we have correlated  
4 core electrons in the solution of ground state CC equations for all calculations presented  
5 here.  
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9 All calculations presented here have been performed using the CFOUR program pack-  
10 age.<sup>66,80-83,85-87</sup> Relativistic effects have been included using spin-free exact two-component  
11 theory in its one-electron variant (SFX2C-1e)<sup>78,79</sup> with correlation-consistent basis sets<sup>73-75</sup>  
12 recontracted for the SFX2C-1e scheme. The detailed information about the SFX2C-1e re-  
13 contracted basis sets can be found at [www.cfour.de](http://www.cfour.de). The experimental equilibrium bond  
14 lengths<sup>88</sup> have been used in calculations for diatomic molecules, while the structures opti-  
15 mized at SFX2C-1e-CCSD(T)/cc-pCVQZ level have been used for all polyatomic molecules.  
16 The geometrical parameters are documented in the supplementary material. In order to  
17 compare the performance of CVS-EOMIP-CCSD and full EOMIP-CCSD, we carried out  
18 CVS-EOMIP-CCSD and full EOMIP-CCSD calculations for 1s ionization energies in HF,  
19 F<sub>2</sub>, N<sub>2</sub>, CO, and H<sub>2</sub>O using the aug-cc-pCVXZ (X=T, Q, 5) basis sets. To compare the  
20 performance of basis sets with and without diffuse functions, CVS-EOMIP-CCSDT calcu-  
21 lations have been performed for 1s ionization energies in HF, CO, N<sub>2</sub>, F<sub>2</sub>, and H<sub>2</sub>O using  
22 aug-cc-pCVXZ (X=D, T, Q, 5) and cc-pCVXZ (X=D, T, Q, 5) sets. The performance of  
23 CCSD and CCSDT methods is studied by performing CVS-EOMIP-CCSD and CCSDT cal-  
24 culations of 1s ionization energies in HF, CO, N<sub>2</sub>, F<sub>2</sub>, and H<sub>2</sub>O using cc-pCVXZ (X=T, Q, 5)  
25 sets and in C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, CH<sub>4</sub>, CH<sub>2</sub>O, CO<sub>2</sub>, NNO, NH<sub>3</sub>, HCN and CH<sub>3</sub>OH using cc-pCVTZ  
26 and cc-pCVQZ basis sets. Corrections from quadruple excitations have been obtained as  
27 the difference between CVS-EOMIP-CCSDTQ and CVS-EOMIP-CCSDT results using the  
28 cc-pCVTZ basis sets for HF, F<sub>2</sub>, N<sub>2</sub>, CO, H<sub>2</sub>O and using the cc-pVTZ basis sets for the  
29 other polyatomic molecules. We mention that the experimental ionization energies<sup>89</sup> used in  
30 the comparison are all taken from experimental studies without vibrational resolution and  
31 thus they approximately correspond to vertical ionization energies. Therefore, it is justi-  
32 fied to compare the computed vertical ionization energies with these experimental results.  
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3 Finally, CVS-EOMIP-CCSD calculations using cc-pCVTZ and cc-pCVQZ basis sets and  
4 CVS-EOMIP-CCSDT/cc-pCVTZ calculations have been carried out for the CH<sub>3</sub>CN and  
5 CH<sub>3</sub>NC molecules. All EOMIP-CC and CVS-EOMIP-CC calculations have been tightly  
6 converged; the convergence threshold for the maximum norm of the elements in the EOMIP  
7 energy-weighted residue vector is 10<sup>-5</sup> a.u., and the variance of ionization energies is below  
8 10<sup>-6</sup> E<sub>h</sub> upon convergence.  
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## 18 3 Results and Discussion

### 19 3.1 CVS-EOMIP-CC versus full EOMIP-CC

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21 As shown in Table 1 and also in Fig. 1, the 1s ionization energies for HF, F<sub>2</sub>, N<sub>2</sub>, CO, and  
22 H<sub>2</sub>O computed at the CVS-EOMIP-CCSD level converge smoothly along aug-cc-pCVXZ  
23 (X=T, Q, 5) sets. In contrast, the basis-set convergence of the full EOMIP-CCSD results  
24 shows significant oscillations for all cases. This irregular performance of the full EOMIP-  
25 CCSD method can be attributed to spurious couplings between the ionized state and high-  
26 lying pure valence ionized states that are accidentally (quasi-)degenerate. Note that the lat-  
27 ter consists of ionization of a valence electron accompanied by an excitation from a valence  
28 orbital to a high-lying virtual orbital and should not significantly contribute to core-ionized  
29 state. For example, the wave function from the full EOMIP-CCSD/aug-cc-pCVQZ calcula-  
30 tion for the fluorine 1s<sup>-1</sup> state of F<sub>2</sub> has a 20% contamination from pure valence ionizations  
31 with similar energies. In other words, when basis sets accidentally cover high-lying (con-  
32 tinuum) valence ionized states that are (quasi-)degenerate to core-ionized states of interest,  
33 unphysical contributions arise and lead to numerical errors in the ionization energies, even  
34 if the full EOMIP-CCSD equations are tightly converged. Therefore, the CVS scheme not  
35 only expedites the convergence of the EOMIP-CC equations, but also excludes spurious in-  
36 teractions between core-ionized and valence continuum states. Hence, the CVS-EOMIP-CC  
37 methods are better than the corresponding full CVS-EOMIP-CC methods for calculations of  
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3 core-ionized states. Therefore, we have adopted the CVS scheme in all following calculations.  
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### 7 **3.2 Effects of diffuse functions on computed ionization energies**

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10 Diffuse functions do not contribute much to K-edge ionization energies, as core ionization  
11 is a spatially localized process. It is demonstrated in Table 2 that CVS-EOMIP-CCSDT  
12 results using aug-cc-pCVXZ (X=D, T, Q, 5) and cc-pCVXZ (X=D, T, Q, 5) sets converge  
13 to essentially the same values; the differences between aug-cc-pCV5Z and cc-pCV5Z results  
14 are at most 0.03 eV. Interestingly, the cc-pCVXZ results seem to converge more rapidly than  
15 the aug-cc-pCVXZ ones. All cc-pCVTZ results are within 0.12 eV in comparison with cc-  
16 pCV5Z or aug-cc-pCV5Z results, while the aug-cc-pCVTZ results deviate more substantially  
17 from the 5Z results. Double-zeta basis sets (aug-cc-pCVDZ and cc-pCVDZ) do not provide  
18 accurate results for K-edge ionization energies and show errors greater than 1 eV for all cases.  
19 The use of triple-zeta basis lowers basis-set errors by an order of magnitude. Based on the  
20 above observations and analyses of basis-set effects, the cc-pCVXZ (X=T, Q, 5) basis sets  
21 have been used in the following studies on the convergence of CVS-EOMIP-CC methods  
22 with respect to the excitation rank.  
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### 37 **3.3 Accuracy of CVS-EOMIP-CCSD and CVS-EOMIP-CCSDT**

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40 As shown in Tables 3, 5, and 6, the deviation of CVS-EOMIP-CCSD K-edge ionization  
41 energies from experimental values is typically 1-3 eV, while the corresponding deviations for  
42 chemical shifts are usually less than 0.5 eV. Here the chemical shifts for the 1s ionization  
43 energies of C, N, O, and F are given as the differences with respect to those in CO, N<sub>2</sub>, CO,  
44 and HF, respectively. N<sub>2</sub>O appears to be a difficult case, in which the chemical shifts of the  
45 terminal nitrogen and the middle nitrogen with respect to N<sub>2</sub> still amount to 0.74 and 0.99  
46 eV, respectively (see Table 6). The relatively slow convergence of the computed ionization  
47 energies with respect to the excitation rank within CVS-EOMIP-CC for N<sub>2</sub>O indicates the  
48 strong orbital relaxation induced by the creation of the core hole in this molecule. The linear  
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3 parametrization of the  $\hat{R}$  operator in EOMCC does not efficiently take orbital rotation into  
4 account. Consequently, higher excitations are required when aiming at quantitative results.  
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6 It can be seen from Tables 3, 5, and 6 that agreement between theory and experiment is  
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8 much improved when triple excitations are included. Most CVS-EOMIP-CCSDT results are  
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10 within 0.3 eV in comparison with experimental values. The middle nitrogen in N<sub>2</sub>O remains  
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12 the most difficult case, with the deviation between CVS-EOMIP-CCSDT and experiment  
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14 still higher than 0.5 eV.  
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17 We mention that, interestingly, the basis-set convergence of the CCSDT results could  
18  
19 be quite different from CCSD. For example, the CVS-EOMIP-CCSD/cc-pCVTZ result for  
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21 F 1s ionization energies in HF is 0.22 eV smaller than the CVS-EOMIP-CCSD/cc-pCV5Z  
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23 result, while the CVS-EOMIP-CCSDT/cc-pCVTZ value is 0.02 eV higher than the CVS-  
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25 EOMIP-CCSDT/cc-pCV5Z result. Therefore, additivity schemes that augment lower-level  
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27 CC results obtained using larger basis sets with corrections from high-level CC calculations  
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29 using smaller basis sets should be used with care for core ionization energies, especially when  
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31 aiming at high accuracy. Despite the profound coupling between electron-correlation and  
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33 basis-set effects, basis-set convergence for core-ionization energies is pretty fast. The cc-  
34  
35 pCVTZ basis in general provides accurate treatment of basis-set effects, while CVS-EOMIP-  
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37 CCSDT/cc-pCVQZ results are within 0.02 eV in comparison with those of CVS-EOMIP-  
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39 CCSDT/cc-pCV5Z.  
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### 43 3.4 Quadruples corrections

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45 For all diatomic molecules in the benchmark set as well as for H<sub>2</sub>O, effects of quadruple  
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47 excitations have been studied at the CVS-EOMIP-CCSDTQ/cc-pCVTZ level and are sum-  
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49 marized in Table 3. The absolute values for the quadruples corrections to K-edge ionization  
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51 energies in these small molecules range from 0.08 to 0.23 eV, about an order of magnitude  
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53 smaller than the corresponding triples corrections. As it is a reasonable assumption that  
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55 corrections from even higher excitations are smaller, the CVS-EOMIP-CCSDTQ results for  
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3 K-edge ionization energies are expected to be very close to the corresponding FCI results.  
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5 As CVS-EOMIP-CCSDTQ/cc-pCVTZ is still too expensive for other polyatomic molecules  
6 in the benchmark set, we have investigated the dependence of quadruples corrections to core-  
7 correlating functions in the basis sets. In Table 4 we summarize the computed quadruples  
8 corrections using the cc-pCVTZ and cc-pVTZ basis sets as well as a combination of cc-  
9 pCVTZ and cc-pVTZ, in which cc-pCVTZ is used for the targeted atom and cc-pVTZ is  
10 used for all other atoms. The core-correlating functions on other atomic centers seem to have  
11 negligible contributions, as the cc-pCVTZ/cc-pVTZ results are essentially indistinguishable  
12 from cc-pCVTZ results. The cc-pVTZ results for absolute core-ionization energies are 0.2-0.5  
13 eV lower than the cc-pCVTZ ones, while cc-pVTZ calculations seem to provide reasonably  
14 good estimates for quadruples corrections. We have obtained quadruples corrections for  
15 all other polyatomic molecules except CH<sub>3</sub>OH using the cc-pVTZ basis and the results are  
16 presented in Table 5. Computational results with inclusion of quadruples corrections show  
17 a standard deviation of 0.10 eV from experiment and can be regarded as essentially quan-  
18 titative. For the middle nitrogen in N<sub>2</sub>O, the quadruples correction amounts to -0.31 eV,  
19 and the inclusion reduces the deviation with respect to experiment from 0.54 eV to 0.23  
20 eV. The excellent agreement between CVS-EOMIP-CC results with inclusion of quadruple  
21 excitations and experimental values indicates that in calculations of core-ionization energies  
22 the approximation of neglecting the continuum part of the wave function in the CVS scheme  
23 is numerically insignificant.  
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### 45 **3.5 Carbon 1s ionization energies in CH<sub>3</sub>CN and CH<sub>3</sub>NC**

46 CVS-EOMIP-CCSD/cc-pCVTZ, CVS-EOMIP-CCSD/cc-pCVQZ, and CVS-EOMIP-CCSDT/cc-  
47 pCVTZ calculations have been carried out for CH<sub>3</sub>CN and CH<sub>3</sub>NC and compared with two  
48 different sets of experimental results available in the literature.<sup>90,91</sup> As shown in Table 7,  
49 comparison between CVS-EOMIP-CCSD/cc-pCVTZ and CVS-EOMIP-CCSD/cc-pCVQZ  
50 confirms that basis-set effects beyond cc-pCVTZ play a minor role. On the other hand,  
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triples corrections are significant. Although the absolute magnitude for the triples correction to the relative shift between the two carbons in  $\text{CH}_3\text{CN}$  is only 0.17 eV, the inclusion of triples corrections reverses the ordering of carbon 1s ionization energies for the methyl carbon and the cyano carbon. The computational results (292.90 eV for cyano carbon and 292.81 eV for methyl carbon with a relative shift of 0.09 eV) differ significantly from the more recent experimental results (292.45 eV for cyano carbon and 292.98 eV for methyl carbon with a relative shift of -0.53 eV). Since the triples correction to this relative shift is only 0.17 eV, we do not expect the corresponding quadruples correction to be close to the difference of -0.62 eV between the computational and experimental results. Interestingly, the computational results qualitatively agree with an earlier experiment with a lower resolution (293.2 for cyano carbon and 293.1 for methyl carbon with a relative shift of 0.1 eV). It is also observed that, for  $\text{CH}_3\text{NC}$ , our CVS-EOMIP-CCSDT/cc-pCVTZ results agree very well with the more recent experimental study, and differ considerably from the earlier ones. We would suggest an experimental re-investigation of  $\text{CH}_3\text{CN}$  to settle these issues.

## 4 Conclusion

The present manuscript reports benchmark calculations for K-edge ionization energies in C, N, O, F using core-valence-separated (CVS) equation-of-motion ionization-potential coupled-cluster (EOMIP-CC) methods. It is shown that the CVS scheme excludes spurious couplings between core-ionized states and valence continuum states and thus the CVS-EOMIP-CC methods turn out to be better than the parent EOMIP-CC methods in terms of numerical accuracy. Convergence of computed K-edge ionization energies within the hierarchy of CVS-EOMIP-CC methods has been carefully studied. Essentially quantitative agreement between computed and experimental results is obtained when quadruples contributions are included. We mention that the magnitude of the remaining errors of CCSDTQ for the electronic contributions to K-edge ionization energies are comparable with or even smaller than that of

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3 vibrational corrections. Therefore, computational studies with vibrational corrections taken  
4 into account and the comparison of the corresponding results with vibrationally resolved  
5 experimental results would be of great interest for future studies. Finally, computational  
6 results for carbon 1s ionization energies in CH<sub>3</sub>CN and CH<sub>3</sub>NC suggest an experimental  
7 re-investigation of these molecules.  
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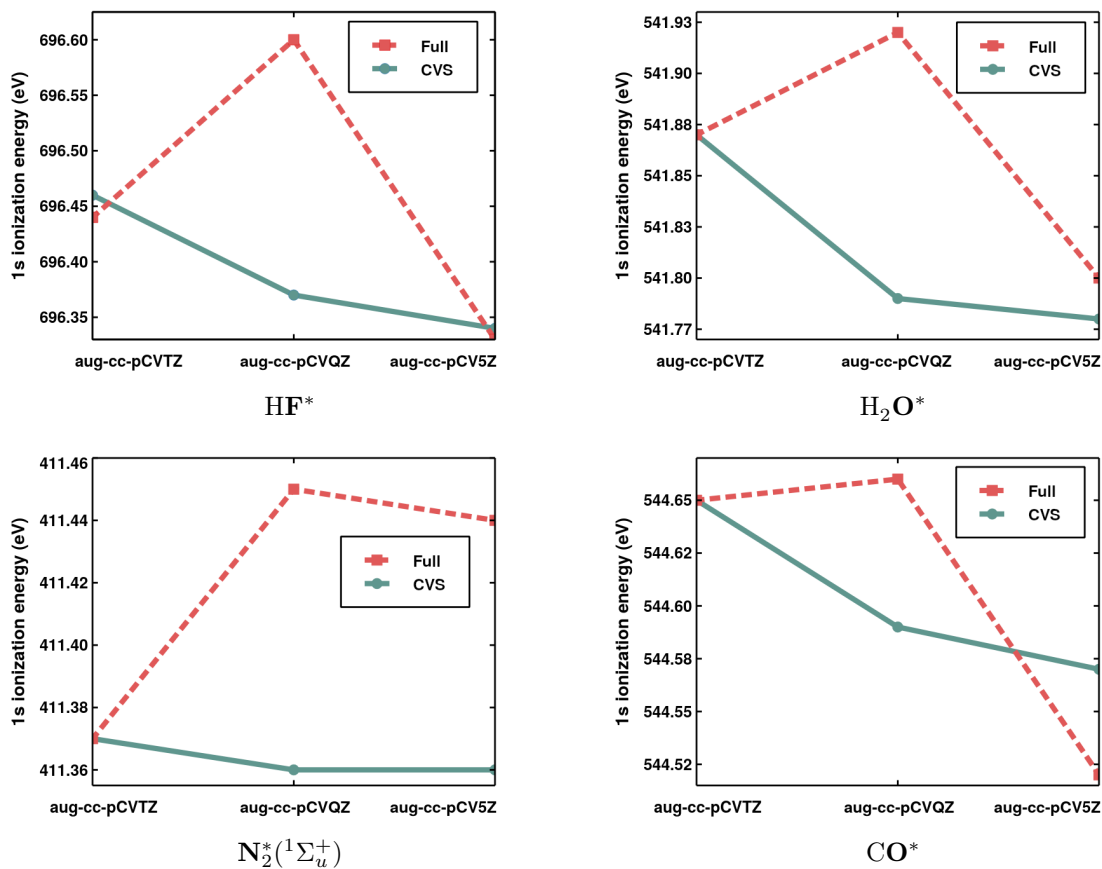


Figure 1: 1s ionization energies (in eV) computed at the EOMIP-CCSD level for the atoms in bold letter marked with an asterisk. “CVS” denotes the use of the core-valence separation scheme. “Full” stands for the solution of EOMIP-CCSD equations in the full singles and doubles space.



Table 1: 1s ionization energies (in eV) computed at the EOMIP-CCSD level for the atoms in bold letter marked with an asterisk. “CVS” denotes the use of the core-valence separation scheme, while “full” stands for the solution of EOMIP-CCSD equations in the full singles and doubles space.

		aug-cc-pCVTZ	aug-cc-pCVQZ	aug-cc-pCV5Z
<b>HF*</b>	full	696.44	696.60	696.33
	CVS	696.46	696.37	696.34
<b>F<sub>2</sub>*(<sup>1</sup>Σ<sub>g</sub><sup>+</sup>)</b>	full	699.20	699.59	699.07
	CVS	699.23	699.14	699.12
<b>F<sub>2</sub>*(<sup>1</sup>Σ<sub>u</sub><sup>+</sup>)</b>	full	699.19	699.03	699.06
	CVS	699.22	699.13	699.11
<b>N<sub>2</sub>*(<sup>1</sup>Σ<sub>g</sub><sup>+</sup>)</b>	full	411.47	411.51	411.48
	CVS	411.47	411.46	411.46
<b>N<sub>2</sub>*(<sup>1</sup>Σ<sub>u</sub><sup>+</sup>)</b>	full	411.37	411.45	411.44
	CVS	411.37	411.36	411.36
<b>C*O</b>	full	297.73	297.73	297.74
	CVS	297.72	297.71	297.72
<b>CO*</b>	full	544.65	544.66	544.52
	CVS	544.65	544.59	544.57
<b>H<sub>2</sub>O*</b>	full	541.87	541.92	541.80
	CVS	541.87	541.79	541.78

Table 2: 1s ionization energies (in eV) computed at the CVS-EOMIP-CCSDT level for the atoms in bold letter marked with an asterisk. “CXZ” and “ACXZ” (X=D, T, Q, 5) represent cc-pCVXZ and aug-cc-pCVXZ sets, respectively. The SFX2C-1e scheme has been used to treat scalar-relativistic effects.

Molecule	ACDZ	ACTZ	ACQZ	AC5Z	CDZ	CTZ	CQZ	C5Z
<b>HF*</b>	696.66	694.45	694.28	694.23	695.98	694.22	694.19	694.20
<b>C*O</b>	297.85	296.53	296.46	296.45	297.83	296.47	296.44	296.45
<b>CO*</b>	544.50	542.64	542.50	542.46	544.29	542.57	542.48	542.46
<b>N<sub>2</sub><sup>*</sup>(<sup>1</sup>Σ<sub>g</sub><sup>+</sup>)</b>	411.89	410.20	410.11	410.09	411.69	410.11	410.08	410.07
<b>N<sub>2</sub><sup>*</sup>(<sup>1</sup>Σ<sub>u</sub><sup>+</sup>)</b>	411.80	410.11	410.03	410.01	411.60	410.03	409.99	409.99
<b>F<sub>2</sub><sup>*</sup>(<sup>1</sup>Σ<sub>g</sub><sup>+</sup>)</b>	699.10	696.90	696.74	696.70	698.59	696.73	696.67	696.67
<b>F<sub>2</sub><sup>*</sup>(<sup>1</sup>Σ<sub>u</sub><sup>+</sup>)</b>	699.09	696.89	696.73	696.69	698.58	696.72	696.66	696.66
<b>H<sub>2</sub>O*</b>	541.90	540.00	539.85	539.81	541.36	539.79	539.76	539.78

Table 3: 1s ionization energies (in eV) for the atoms in bold letter marked with an asterisk. “CXZ” (X=T, Q, 5) denotes cc-pCVXZ sets. The deviations from experimental values are enclosed in parentheses. The core-valence separation scheme has been used. Scalar-relativistic effects have been taken into account using the SFX2C-1e scheme.

Molecule	EOMIP-CCSD			EOMIP-CCSDT			EOMIP-CCSDTQ	total <sup>a</sup>	Exp. <sup>89</sup>
	CTZ	CQZ	C5Z	CTZ	CQZ	C5Z	CTZ		
<b>HF*</b>	696.09	696.23	696.31	694.22	694.19	694.20	694.45	694.44	694.23
	(1.86)	(2.00)	(2.08)	(-0.01)	(-0.04)	(-0.03)	(0.22)	(0.21)	
<b>C*O</b>	297.64	297.69	297.71	296.47	296.44	296.45	296.30	296.27	296.21
	(1.43)	(1.48)	(1.50)	(0.26)	(0.23)	(0.24)	(0.09)	(0.06)	
<b>CO*</b>	544.57	544.56	544.57	542.57	542.48	542.46	542.68	542.57	542.55
	(2.02)	(2.01)	(2.02)	(0.02)	(-0.07)	(-0.09)	(0.13)	(0.02)	
<b>N<sub>2</sub><sup>*(1Σ<sub>g</sub><sup>+</sup>)</sup></b>	411.35	411.41	411.43	410.11	410.08	410.07	410.03	409.99	409.98
	(1.37)	(1.43)	(1.45)	(0.13)	(0.10)	(0.09)	(0.05)	(0.01)	
<b>N<sub>2</sub><sup>*(1Σ<sub>u</sub><sup>+</sup>)</sup></b>	411.25	411.31	411.33	410.03	409.99	409.99	409.95	409.91	409.98
	(1.27)	(1.33)	(1.35)	(0.05)	(0.01)	(0.01)	(-0.03)	(-0.07)	
<b>F<sub>2</sub><sup>*(1Σ<sub>g</sub><sup>+</sup>)</sup></b>	699.01	699.06	699.09	696.73	696.67	696.67	696.82	696.75	696.69
	(2.32)	(2.37)	(2.40)	(0.04)	(-0.02)	(-0.02)	(0.13)	(0.06)	
<b>F<sub>2</sub><sup>*(1Σ<sub>u</sub><sup>+</sup>)</sup></b>	699.00	699.05	699.08	696.72	696.66	696.66	696.81	696.75	696.69
	(2.31)	(2.36)	(2.39)	(0.03)	(-0.03)	(-0.03)	(0.12)	(0.06)	
<b>H<sub>2</sub>O*</b>	541.53	541.65	541.74	539.79	539.76	539.78	539.99	539.98	539.90
	(1.63)	(1.75)	(1.84)	(-0.11)	(-0.14)	(-0.11)	(0.09)	(0.08)	

<sup>a</sup> CCSDT/cc-pCV5Z results augmented with quadruples corrections obtained using the cc-pCVTZ basis.

Table 4: 1s ionization energies (in eV) for the atoms in bold letter marked with an asterisk computed using CVS-EOMIP-CC methods.

Molecules	Method	cc-pCVTZ	cc-pCVTZ/cc-pVTZ <sup>a</sup>	cc-pVTZ
<b>C*O</b>	CCSDT	296.47	296.47	295.97
	CCSDTQ	296.30	296.29	295.81
	$\Delta_Q$	-0.17	-0.17	-0.16
<b>CO*</b>	CCSDT	542.57	542.57	542.21
	CCSDTQ	542.68	542.68	542.34
	$\Delta_Q$	0.11	0.11	0.13
<b>N*<sub>2</sub>(<math>\Sigma_g^+</math>)</b>	CCSDT	410.11	410.11	409.68
	CCSDTQ	410.03	410.03	409.62
	$\Delta_Q$	-0.08	-0.08	-0.07
<b>N*<sub>2</sub>(<math>\Sigma_u^+</math>)</b>	CCSDT	410.03	410.03	409.60
	CCSDTQ	409.95	409.95	409.53
	$\Delta_Q$	-0.08	-0.08	-0.06
<b>F*<sub>2</sub>(<math>\Sigma_g^+</math>)</b>	CCSDT	696.73	696.73	696.45
	CCSDTQ	696.82	696.82	696.57
	$\Delta_Q$	0.09	0.09	0.13
<b>F*<sub>2</sub>(<math>\Sigma_u^+</math>)</b>	CCSDT	696.72	696.72	696.44
	CCSDTQ	696.81	696.81	696.56
	$\Delta_Q$	0.09	0.09	0.13
<b>HF*</b>	CCSDT	694.22	694.22	693.93
	CCSDTQ	694.45	694.45	694.19
	$\Delta_Q$	0.23	0.23	0.26

<sup>a</sup> cc-pCVTZ basis for the targeted atom and cc-pVTZ basis for the other atoms.

Table 5: Computed 1s ionization energies (in eV) for the atoms in bold letter marked with an asterisk. CXZ (X=T,Q) denote cc-pCVXZ basis sets. The core-valence separation scheme has been used, and relativistic effects have been treated using the SFX2C-1e scheme. “MAE” represents the mean absolute deviation with respect to experimental values.

	EOMIP-CCSD		EOMIP-CCSDT		$\Delta_Q^a$	Best theory <sup>b</sup>	Exp. <sup>89</sup>	$\Delta(\text{Theory-Exp})$
	CTZ	CQZ	CTZ	CQZ				
<b>C</b> <sub>2</sub> H <sub>4</sub> (A <sub>g</sub> )	292.32	292.32	290.89	290.81	0.00	290.81	290.82	-0.01
<b>C</b> <sub>2</sub> H <sub>4</sub> (B <sub>2u</sub> )	292.26	292.27	290.85	290.76	0.00	290.77	290.82	-0.05
<b>C</b> <sub>2</sub> H <sub>2</sub> ( <sup>1</sup> Σ <sub>g</sub> <sup>+</sup> )	292.72	292.73	291.45	291.36	-0.06	291.31	291.14	0.17
<b>C</b> <sub>2</sub> H <sub>2</sub> ( <sup>1</sup> Σ <sub>u</sub> <sup>+</sup> )	292.62	292.63	291.36	291.28	-0.05	291.22	291.14	0.08
<b>C</b> *H <sub>4</sub>	292.07	292.04	290.86	290.75	0.05	290.80	290.91	-0.11
CH <sub>2</sub> O*	541.68	541.70	539.44	539.36	0.12	539.48	539.48	0.00
<b>C</b> *H <sub>2</sub> O	295.94	295.99	294.62	294.58	-0.12	294.46	294.47	-0.01
CO <sub>2</sub> *	543.70	543.73	541.40	541.35	-0.01	541.34	541.28	0.06
<b>C</b> *O <sub>2</sub>	299.52	299.59	298.03	298.02	-0.26	297.76	297.69	0.07
NNO*	543.92	543.96	541.63	541.57	-0.02	541.55	541.42	0.13
NN*O	414.90	414.96	413.15	413.13	-0.31	412.82	412.59	0.23
N*NO	410.76	410.83	408.92	408.90	-0.11	408.79	408.71	0.08
N*H <sub>3</sub>	407.04	407.13	405.55	405.51	0.14	405.65	405.56	0.09
HCN*	408.45	408.47	406.88	406.81	0.01	406.82	406.78	0.04
HC*N	294.66	294.68	293.59	293.53	-0.12	293.41	293.40	0.01
CH <sub>3</sub> O*H	541.05	541.11	539.00	538.95	-	-	539.11	-0.16
<b>C</b> *H <sub>3</sub> OH	293.76	293.79	292.47	292.41	-	-	292.43	-0.02
MAE	1.74	1.78	0.16	0.15	-	0.08	-	-

<sup>a</sup> Quadruples corrections obtained using the cc-pVTZ basis.

<sup>b</sup> CCSDT/cc-pCVQZ results augmented with quadruples corrections obtained using the cc-pVTZ basis.

Table 6: Chemical shifts (in eV) of C and O 1s ionization energies (IEs) relative to CO, N 1s IEs relative to N<sub>2</sub>, and F 1s IEs relative to HF. The cc-pCVQZ basis has been used in all CVS-EOMIP-CCSD and CCSDT calculations, while all quadruples corrections have been obtained using the cc-pVTZ basis. The deviations between computation and experiment are given in parenthesis.

	Experiment	CCSD	CCSDT	CCSDTQ
<b>C*O</b>	296.21	297.69	296.44	296.28
<b>C*H<sub>4</sub></b>	-5.30	-5.64(-0.34)	-5.69(-0.39)	-5.48(-0.18)
<b>C<sub>2</sub>*H<sub>2</sub></b>	-5.07	-5.01(0.06)	-5.12(-0.05) <sup>a</sup>	-5.01(0.06) <sup>a</sup>
<b>C<sub>2</sub>*H<sub>4</sub></b>	-5.39	-5.39(0.00)	-5.65(-0.26) <sup>a</sup>	-5.49(-0.10) <sup>a</sup>
<b>C*H<sub>2</sub>O</b>	-1.74	-1.70(0.04)	-1.86(-0.12)	-1.82(-0.08)
<b>C*O<sub>2</sub></b>	1.48	1.90(0.42)	1.58(0.10)	1.48(0.00)
<b>HC*N</b>	-2.81	-3.00(-0.19)	-2.91(-0.10)	-2.87(-0.06)
<b>C*H<sub>3</sub>OH</b>	-3.78	-3.90(-0.12)	-4.03(-0.25)	-
<b>N<sub>2</sub>*</b>	409.98	411.36 <sup>a</sup>	410.03 <sup>a</sup>	409.97 <sup>a</sup>
<b>N*NO</b>	-1.27	-0.53(0.74)	-1.13(0.14)	-1.17(0.10)
<b>NN*O</b>	2.61	3.60(0.99)	3.10(0.49)	2.85(0.24)
<b>N*H<sub>3</sub></b>	-4.42	-4.23(0.19)	-4.52(-0.10)	-4.32(0.10)
<b>HCN*</b>	-3.20	-2.88(0.32)	-3.22(-0.02)	-3.15(0.05)
<b>CO*</b>	542.55	544.56	542.48	542.61
<b>H<sub>2</sub>O*</b>	-2.65	-2.91(-0.26)	-2.71(-0.06)	-2.63(0.02)
<b>CH<sub>2</sub>O*</b>	-3.07	-2.86( 0.21)	-3.12(-0.05)	-3.13(-0.06)
<b>CO<sub>2</sub>*</b>	-1.27	-0.83( 0.44)	-1.13( 0.14)	-1.27(0.00)
<b>N<sub>2</sub>O*</b>	-1.13	-0.60( 0.53)	-0.90( 0.23)	-1.06(0.07)
<b>CH<sub>3</sub>O*H</b>	-3.44	-3.45(-0.01)	-3.53(-0.09)	-
<b>HF*</b>	694.23	696.23	694.19	694.45
<b>F<sub>2</sub>*</b>	2.46	2.82(0.36) <sup>a</sup>	2.47(0.01) <sup>a</sup>	2.34(-0.12) <sup>a</sup>

<sup>a</sup> An average of gerade and ungerade states.

Table 7: 1s ionization energies (in eV) for the atoms in bold letter marked with an asterisk.

	Exp. <sup>91</sup>	Exp. <sup>90</sup>	CVS-EOMIP-CCSD		CVS-EOMIP-CCSDT
			cc-pCVTZ	cc-pCVQZ	cc-pCVTZ
CH <sub>3</sub> <b>C</b> *N	292.45	293.2	294.06	294.09	292.90
<b>C</b> *H <sub>3</sub> CN	292.98	293.1	294.13	294.13	292.81
CH <sub>3</sub> CN*	405.64	405.9	407.52	407.54	405.71
CH <sub>3</sub> NC*	292.37	293.8	294.07	294.12	292.35
<b>C</b> *H <sub>3</sub> NC	293.35	293.1	294.78	294.78	293.41
CH <sub>3</sub> <b>N</b> *C	406.67	407.1	408.38	408.40	407.02

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## Supporting Information Available

The geometrical parameters for the molecules used in the present study have been compiled and given in the supplementary material. This material is available free of charge via the Internet at <http://pubs.acs.org/>.

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## Graphical TOC Entry

