

## CEPA calculations on open-shell molecules. VI. The first ionization potential of HCO

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According to an investigation by Dyke et al. (1980) HCO seems to be one of the rare cases in which the correlation energy of the neutral molecule is smaller (in absolute value) than that of the first monocation, such that the  $\Delta$ SCF method yields a value for the first vertical ionization potential ( $IP_v$ ) which is larger than the experimental value. In order to understand this observation we have performed a series of SCF and CEPA calculations on HCO and  $HCO^+$  using as many as ten different orbital basis sets. The best  $\Delta$ SCF result for  $IP_v$  is 9.24 eV, i.e. slightly smaller than the "experimental electronic"  $IP_v$  of 9.38 eV. Inclusion of electron correlation lowers  $IP_v$  as long as small basis sets are used, the convergence with increasing basis size is very slow. Extrapolation to a complete basis leads to a CEPA estimate of  $9.26 \pm 0.10$  eV for  $IP_v$  (and  $8.05 \pm 0.10$  eV for the adiabatic IP) which shows that the correlation contribution to  $IP_v$  is indeed very small. The reason for this is that the gain in correlation energy in HCO due to the presence of the unpaired electron is compensated by a loss of core correlation energy since the low-lying antibonding in-plane C–O– $\pi$ -orbital is only partially available for excitation in HCO, but fully available in  $HCO^+$ .

**Key words:** Formyl radical—Ionization potential—Electron correlation effects.

### 1. Introduction

The first level of approximation in *ab initio* calculations of molecular ionization potentials (IP) usually is either Koopmans' theorem [1] or the  $\Delta$ SCF method [2]. In the latter scheme, separate SCF calculations are performed for the neutral molecule and the ion, i.e. reorganization effects are taken care of, but electron

correlation effects are completely neglected. Since the correlation energy of the neutral molecule is usually larger (in absolute value) than that of the ion which has one electron less,  $\Delta$ SCF results for first (lowest) IPs are in general too small. Typical errors are 0.5–1.0 eV, but much larger deviations from experiment may also be found. The validity of Koopmans' theorem, on the other hand, depends on a partial cancellation of reorganization and correlation effects [3]. Since the reorganization energy generally is larger than the difference in the correlation energies of neutral molecule and ion, Koopmans' theorem generally yields too large values for first IPs. Typical examples can be found in a review on applications of *ab initio* methods to the calculation of molecular properties [4].

Recently, Dyke et al. [5] studied the first IP of HCO experimentally, using photoelectron spectroscopy. The first vertical IP was measured as  $9.31 \pm 0.01$  eV, with the aid of Franck–Condon calculations the first adiabatic IP was estimated as  $8.27 \pm 0.01$  eV. In addition to the experimental determination, the authors also reported on  $\Delta$ SCF calculations; the vertical IP was obtained as 9.44 eV (calculated with a *DZ + dp* STO basis set), i.e. larger than the experimental value. This means that the correlation energy of  $\text{HCO}^+$  has to be larger (in absolute value) than that of HCO, both taken at the HCO equilibrium geometry. Thus, HCO seems to be one of the rare exceptions, in which the  $\Delta$ SCF result for the first vertical IP is too large. (Semiempirical estimates of the correlation energy difference between HCO and  $\text{HCO}^+$ , using the method of Liu and Verhaegen [6, 7], reduced the high  $\Delta$ SCF value to 9.16 eV [5], in reasonable agreement with the measured value).

In order to understand this unusual result we have performed a series of SCF and CEPA calculations on HCO (at its equilibrium geometry) and  $\text{HCO}^+$  (both at its own and at the HCO equilibrium geometry). The main objective of the present study is – apart from obtaining a reliable *ab initio* value for the correlation contribution  $\Delta E_{\text{corr}}$  to the first IP – an analysis of the different effects that contribute to  $\Delta E_{\text{corr}}$ . It turned out the  $\Delta E_{\text{corr}}$  depends very strongly on the basis set used, therefore we have explored a large number of different basis sets and tried to perform an extrapolation to the limit of a complete basis.

## 2. Details of the calculations

For HCO we used the experimental equilibrium geometry as determined by microwave spectroscopy [8]:  $R_{\text{CO}} = 1.171$  Å,  $R_{\text{CH}} = 1.110$  Å,  $\vartheta = 127.426^\circ$ . For the equilibrium geometry of  $\text{HCO}^+$  we took the values determined by Bruna et al. on SCF-level [9]:  $R_{\text{CO}} = 1.108$  Å,  $R_{\text{CH}} = 1.085$  Å,  $\vartheta = 180^\circ$ . They are quite close to results of other calculations as well as to the experimental microwave data as quoted in [5]. No attempt has been made to further optimize any of the geometrical parameters.

In its bent equilibrium geometry HCO has a  ${}^2A'$  ground state with the electronic configuration

$$\dots (5a')^2(6a')^2(1a'')^2(7a')^1$$

i.e. with a half-filled  $7a'$  orbital. The first IP corresponds to the ionization from the  $7a'$  orbital which gives a  ${}^1A'$  state that relaxes to the linear equilibrium geometry of  $\text{HCO}^+$  in its  ${}^1\Sigma^+$  ground state.

All our SCF, CI, and CEPA calculations have been performed as described in part I of this series [10], the CEPA-2 variant and canonical SCF-orbitals were used throughout. The  $1s$  electrons on O and C were not included in the correlation treatment. For all basis sets and geometies correlation energies have been calculated without and with inclusion of singly excited configurations (CI(D), CEPA(D) and CI(SD), CEPA(SD), respectively). We shall not document all the results of these variants here, since the differences are generally unsubstantial and do not change the general conclusions. The CEPA(SD) results are considered to be the most reliable ones, though in some cases better agreement with experiment may be achieved with one of the other variants.

Our basis sets consisted of Gaussian lobe functions with exponents and contraction coefficients as published by Huzinaga [11, 12]. We started from conventional double-zeta (DZ), triple-zeta (TZ) and extended (ext.)  $s,p$  sets which were augmented step by step by higher angular basis functions ( $d$  and  $f$  on C, O;  $p$  on H) and in one case by more diffuse functions. The exponents of the polarization functions were chosen close to those optimized previously [13]. The details of the ten basis sets used in the subsequent calculations are given in Table 1.

A short comment on the use of Koopmans' theorem is necessary: In its usual form [1] it is only valid for closed-shell states, therefore it cannot be applied to HCO which has an open-shell  ${}^2A'$  ground state. However, also in open-shell SCF theory it is possible to define the orbital energies—the definition of which is not unique in SCF theory—as to correspond to the (negative) ionization energies

**Table 1.** Basis sets for HCO and  $\text{HCO}^+$

Basis	Size	$sp^a$	Additional functions
DZ	22	7,3/3 $\rightarrow$ 4,2/2	—
DZ + $dp$	35	as DZ	$d_o(1.25)$ , $d_c(0.80)$ , $p_H(0.65)$
TZ	31	9,5/5 $\rightarrow$ 5,3/3	—
TZ + $d_\delta p^b$	38	as TZ	$d_o(1.25)$ , $d_c(0.80)$ , $p_H(0.65)$
TZ + $dp$	44	as TZ	as TZ + $d_\delta p$
TZ + $rdp^c$	52	as TZ	as TZ + $dp$
		$s_o(0.09)$ , $p_o(0.07)$ $s_c(0.05)$ , $p_c(0.04)$	
TZ + $2d1p$	54	as TZ	$d_o(2.0, 0.5)$ , $d_c(1.0, 0.3)$ , $p_H(0.65)$
TZ + $2d1f2p$	71	as TZ	$f_o(1.4)$ , $d_o(2.0, 0.5)$ , $f_c(0.8)$ , $d_c(1.0, 0.3)$ , $p_H(1.3, 0.35)$
ext.	51	12,7/7 $\rightarrow$ 8,5/5	—
ext. + $dp$	64	as ext.	$d_o(1.25)$ , $d_c(0.80)$ , $p_H(0.65)$

<sup>a</sup> 7,3/3 means 7s, 3p on O and C, 3s on H.

<sup>b</sup> Only those  $d$ -components are included which have  $\delta$ -symmetry with respect to the C–O axis.

<sup>c</sup>  $r$  (=Rydberg-type) for diffuse  $s,p$  functions on O and C.

in the same way as this is the case for closed-shell states. For a more detailed discussion the reader is referred to [14]. In our SCF calculations such a definition is used and Koopmans' theorem holds in exactly the same way as for closed-shell states.

### 3. Overall results for the first IP of HCO

We define the ionization potential in the usual way as

$$\text{IP} = E(\text{HCO}^+) - E(\text{HCO}) = \Delta E_{\text{SCF}} + \Delta E_{\text{corr}}$$

$$\Delta E_{\text{corr}} = E_{\text{corr}}(\text{HCO}^+) - E_{\text{corr}}(\text{HCO})$$

Since correlation energies are negative, a negative value of  $\Delta E_{\text{corr}}$  indicates that  $E_{\text{corr}}(\text{HCO}^+)$  is larger in absolute value than  $E_{\text{corr}}(\text{HCO})$  and that correlation reduces the always positive  $\Delta\text{SCF}$  value for the IP.

For a fair comparison between the calculated purely electronic IPs and the observed data which are energy differences between vibrational levels we have to account for the change in the vibrational energies: For HCO, the vibrational fundamentals are known experimentally ( $\nu_1 = 2483 \text{ cm}^{-1}$  [15],  $\nu_2 = 1081 \text{ cm}^{-1}$  [15, 16],  $\nu_3 = 1868 \text{ cm}^{-1}$  [15, 17]) and the zero-point energy is estimated to be 0.337 eV (uncorrected for anharmonicity terms). For  $\text{HCO}^+$ , only  $\nu_1$  has been measured so far ( $\nu_1 = 3088 \text{ cm}^{-1}$  [18]), for  $\nu_2$  and  $\nu_3$  we use the *ab initio* estimates of the harmonic frequencies as calculated by Kraemer et al. [19] (867 and  $2204 \text{ cm}^{-1}$ , respectively; compare also [5, 20]) and obtain a slightly less accurate value of 0.44 eV for the zero-point energy.

From the observed value of 8.27 eV [5] for the first adiabatic IP ( $\text{IP}_a$ ) of HCO and the 0.10 eV for the difference between the zero-point energies of HCO and  $\text{HCO}^+$  we obtain a value of 8.17 eV for the "experimental electronic"  $\text{IP}_a$ . Similarly, we have to add the zero-point energy of the bending vibration of HCO ( $\approx 540 \text{ cm}^{-1} = 0.07 \text{ eV}$ ) to the measured first vertical IP ( $\text{IP}_v$ ) of 9.31 eV [5] in order to get the "experimental electronic"  $\text{IP}_v$  of 9.38 eV. We will compare all our results with these two "experimental electronic" IPs, which have an accuracy of about 0.03 eV (0.01 eV from the measurement [5] and 0.02 eV from our estimate of the zero-point energies).

Table 2 contains our results for the first IP of HCO, corresponding to the  $(7a')^{-1}$  ion, as calculated with the various basis sets of Table 1. The following observations can be made:

a) Koopmans' values for  $\text{IP}_v$  are always higher (10.0–10.8 eV, depending on the basis) than the experimental value. The two DZ basis sets are obviously too small; improvement of the *s*, *p* part (to TZ or ext.) enlarges  $\text{IP}_v$  by about 0.6 eV. Inclusion of polarization functions consistently reduces the *s*, *p* basis set results by about 0.2 eV. Our best results close to 10.65 eV (Koopmans' limit) are by as much as 1.3 eV larger than the experimental value.

Table 2. Calculated first IP of HCO (vertical and adiabatic)

Basis set	HCO Total energy (SCF) (a.u.)	IP(eV) <sup>a</sup>							
		Koopmans' theorem	SCF	CI(D)	CEPA(D)	CI(SD)	CEPA(SD)	exp [5]	
DZ	-113.068399	10.264	9.213	8.562	8.408	8.510	8.326		
DZ + dp	-113.133004	10.031	8.916	8.676	8.547	8.634	8.478		
TZ	-113.211258	10.793	9.470	8.867	8.716	8.820	8.641		
TZ + d <sub>sp</sub>	-113.220988		7.922	7.729	7.724	7.721	7.730		
TZ + dp	-113.273557	10.620	9.448	9.051	8.914	9.004	8.838		
TZ + rdp	-113.275603	10.669	8.060	8.024	8.040	8.010	8.042		
TZ + 2d1p	-113.277386	10.636	9.265	9.050	8.928	9.006	8.857		
TZ + 2d1f2p	-113.281752		7.580	7.685	7.721	7.675	7.729		
ext.	-113.228753	10.823	9.305	9.102	8.987	9.058	8.914		
ext. + dp	-113.287547	10.676	7.622	7.742	7.785	7.732	7.793		
extrapolated <sup>b</sup>		10.65	9.245	9.149	9.053	9.109	8.991		
			7.579	7.806	7.873	7.797	7.885		
			9.235	9.207	9.118	9.169	9.058		
			7.549	7.829	7.909	7.820	7.920		
			9.487	8.915	8.768	8.873	8.702		
			7.935	7.769	7.771	7.766	7.787		
			9.296	9.100	8.983	9.056	8.913		
			7.617	7.740	7.785	7.731	7.796		
			9.25	9.41	9.32	9.37	9.26	9.38 <sup>c</sup>	
			7.55	7.96	8.04	7.95	8.05	8.17 <sup>c</sup>	

<sup>a</sup> First line: vertical IP; second line: adiabatic IP.<sup>b</sup> Estimated error bars:  $\pm 0.02$  eV for Koopmans' and ASCF value of IP<sub>v</sub>;  $\pm 0.05$  eV for ASCF for IP<sub>v</sub>;  $\pm 0.10$  eV for the correlated IP's.<sup>c</sup> "Experimental electronic" IP as defined in text.

b) The  $\Delta$ SCF results are surprisingly close to the experimental value in the case of  $IP_v$ ; they are only about 0.14 eV too small for our best basis set (TZ+2d1f2p). For  $IP_a$ , however, the  $\Delta$ SCF results are about 0.6 eV too small. As for the Koopmans' values, the improvement of the  $s,p$  part of the basis causes an increase, the enlargement of the polarization part a reduction of both  $IP_v$  and  $IP_a$ . From our results with ten basis sets we obtain the following estimate for the infinite basis set limit:  $IP_v = 9.25 \pm 0.02$  eV,  $IP_a = 7.55 \pm 0.05$  eV ( $\Delta$ SCF limit).

c) Inclusion of electron correlation changes  $IP_v$  and  $IP_a$  in a very different manner: The values for  $IP_v$  are strongly reduced, the fair agreement between the  $\Delta$ SCF result and experiment is thus destroyed. The values for  $IP_a$ , on the other hand, increase—at least for the larger basis sets—and the agreement with the experimental  $IP_a$  of 8.17 eV is markedly improved.

If one compares the results of the TZ+ $d_{sp}$  and TZ+ $dp$  basis sets one finds that the  $\sigma$ - and  $\pi$ -components of the  $d$ -sets at C and O are responsible for the reduction of  $IP_v$  and  $IP_a$  on SCF level, whereas the  $\delta$ -components are mainly necessary for correlation.

d) There are slight differences between the four schemes of treating the correlation effects: For  $IP_v$ , the CEPA results are consistently about 0.10 eV lower than the CI results, and those with singles about 0.05 eV lower than without singles. For  $IP_a$ , on the other hand, the singles have no effect and CEPA yields slightly (0.05–0.10 eV) higher results than CI. It is hard to rationalize all these effects; the obvious explanation—size inconsistency effects are larger in the neutral system with one electron more, therefore the CEPA scheme should lead to higher IPs than CI—which seemed to be valid in many systems, e.g. in H<sub>2</sub>O [21], here applies only to  $IP_a$ , not to  $IP_v$ .

Consistently for all basis sets, the CI(D) results for  $IP_v$  are closest to experiment. But this is only the consequence of a cancellation of errors: Both the inclusion of singles and the CEPA estimate of the unlinked cluster contributions lead to a decrease, the improvement of the basis to an increase of the calculated  $IP_v$ . We regard the CEPA(SD) results as the most reliable ones because of their better theoretical justification and since they reproduce the experimental difference between  $IP_v$  and  $IP_a$  (1.21 eV) better than the CI results.

e) The use of as many as ten different basis sets enables us to extrapolate our calculated values for  $IP_v$  and  $IP_a$  to the limit of an infinite basis. From the data of Table 2 one can deduce that the extension of the  $s,p$ -part will probably enhance our best result for  $IP_v$  (TZ+2d1f2p basis) by about 0.10 eV (the improvement from TZ to ext. amounts to about 0.06 eV, both for TZ→ext. and TZ+ $dp$ →ext.+ $dp$ ; another 0.04 eV may be gained upon passing from ext. to an infinite  $s,p$  set). Addition of more and higher angular polarization functions is estimated to lead to a further increase of about 0.10 eV (compare the sequence TZ→TZ+ $dp$ →TZ+2d1p→TZ+2d1f2p). These increments are nearly identical for all four schemes of including correlation effects. A similar estimate can be performed for  $IP_a$ , but it is less reliable since the calculated values for  $IP_a$  depend less systematically on the size of the basis.

The extrapolated CEPA(SD) results (9.26 eV for  $IP_v$ , 8.05 eV for  $IP_a$ ) are still both 0.12 eV below experiment. The main reason is probably a too low estimate of the contribution of higher angular basis functions. The uncertainties due to the approximations inherent in the CEPA scheme, neglect of relativistic effects, neglect of K-L-shell correlation etc. may also account for part of these 0.12 eV.

f) The answer to the question raised in the introduction, whether or not the correlation energy of  $HCO^+$  is larger (in absolute value) than that of HCO, cannot be given unambiguously: In all of our calculations at the equilibrium geometry of HCO, the correlation energy is indeed larger in  $HCO^+$  than in HCO, i.e.  $\Delta E_{corr}$  is negative. If we take our estimates for  $IP_v$  of 9.25 eV on SCF and 9.26 eV on CEPA(SD) level, there is virtually no difference. Only if we compare our  $\Delta SCF$  limit with experiment we find  $\Delta E_{corr}$  to be positive, i.e. the correlation energy to increase (in absolute value) with the number of electrons. For  $IP_a$ , on the other hand,  $\Delta E_{corr}$  is certainly positive.

#### 4. Analysis of the correlation contribution to IP

Our next goal is to understand the unusual fact that  $\Delta E_{corr}$  is negative in all our calculations and close to zero if an extrapolation to infinite basis is performed. To this purpose we have collected in Table 3 the values for  $\Delta E_{corr}$  as calculated with the basis sets of Table 1 (for the four schemes of including correlation effects; at the HCO equilibrium geometry).

While the differences between the four schemes of calculating  $\Delta E_{corr}$  are less important and nearly basis set independent we find a very large and systematic decrease of  $|\Delta E_{corr}|$  upon improving the basis set. The series  $DZ \rightarrow TZ \rightarrow ext.$  as

**Table 3.** Correlation energy difference between  $HCO^+$  and  $HCO^{abc}$

Basis	$\Delta E_{corr}$			
	CI(D)	CEPA(D)	CI(SD)	CEPA(SD)
DZ	-23.91	-29.58	-25.82	-32.60
DZ+ <i>dp</i>	-8.79	-13.53	-10.36	-16.07
TZ	-22.18	-27.71	-23.88	-30.45
TZ+ <i>d<sub>sp</sub></i>	-14.60	-19.63	-16.35	-22.42
TZ+ <i>dp</i>	-7.88	-12.36	-9.52	-15.00
TZ+ <i>rdp</i>	-7.44	-11.70	-9.08	-14.36
TZ+2 <i>d1p</i>	-3.52	-7.02	-5.00	-9.32
TZ+2 <i>d1f2p</i>	-1.05	-4.31	-2.45	-6.54
ext.	-21.04	-26.42	-22.58	-28.85
ext.+ <i>dp</i>	-7.22	-11.52	-8.83	-14.10
extrapolation to infinite basis	+2.7	+0.1	+1.5	-2.0

<sup>a</sup> HCO and  $HCO^+$  at the equilibrium geometry of HCO (i.e. for  $IP_v$ ).

<sup>b</sup>  $\Delta E_{corr}$  positive if  $|E_{corr}(HCO^+)| < |E_{corr}(HCO)|$ .

<sup>c</sup> All entries in mH =  $10^{-3}$  a.u.; 1mH = 0.0272 eV.

well as the series  $DZ + dp \rightarrow TZ + dp \rightarrow \text{ext.} + dp$  shows that the enlargement of the  $s,p$ -part causes only a very small decrease of  $|\Delta E_{\text{corr}}|$ , in the order of  $3 \cdot 10^{-3}$  a.u. The addition of angular terms (e.g. in the series  $TZ \rightarrow TZ + dp \rightarrow TZ + 2d1p \rightarrow TZ + 2d1f2p$ ) is much more important; the reduction of  $|\Delta E_{\text{corr}}|$  in the TZ series amounts to  $23.9 \cdot 10^{-3}$  a.u. = 0.65 eV (CEPA(SD)), that is one order of magnitude more than by the extension of the  $s,p$ -part.

Again we tried to extrapolate  $\Delta E_{\text{corr}}$  to infinite basis size which is a more direct extrapolation than that for  $IP_v$  in the previous section. Assuming that the step from our best result to infinity is as large as the last step ( $TZ + 2d1p \rightarrow TZ + 2p1f2p$  for the angular part,  $TZ + dp \rightarrow \text{ext.} + dp$  for the  $s,p$  part) we obtain the extrapolated values given in Table 3. In agreement with our previous extrapolation for  $IP_v$  we see that  $\Delta E_{\text{corr}}$  for infinite basis is very small.

A similar analysis for the adiabatic correlation energy difference between HCO and  $\text{HCO}^+$  (which is not documented here) shows that now  $\Delta E_{\text{corr}}$  becomes positive as soon as the first  $d,p$  set is added to the  $s,p$ -basis. The dependence of  $\Delta E_{\text{corr}}$  on the basis set is very similar as for the vertical IP. Our extrapolation to infinite basis size gives  $\Delta E_{\text{corr}} = 0.49$  eV which—together with the extrapolated  $\Delta\text{SCF}$  value of 7.55 eV (Table 2)—results in an estimate of 8.04 eV for  $IP_a$ , very similar to the one in Table 2.

A good insight into the origin of  $\Delta E_{\text{corr}}$  is obtained if one decomposes the total (valence shell) correlation energy of HCO into a contribution of the doubly occupied orbitals  $3a'$  to  $1a''$  (called “core” in the following)—which is equivalent to the total correlation energy of  $\text{HCO}^+$ —and a contribution that arises from the correlation between the odd  $7a'$  electron and the doubly occupied orbitals (called “odd electron” correlation). Table 4 contains such a decomposition on CEPA(SD) level.

The two contributions to  $\Delta E_{\text{corr}}$  that result from this decomposition have opposite signs and a completely different dependence on the size of the basis: First, we find a strong reduction of the “core” correlation energy in passing from  $\text{HCO}^+$  to HCO, denoted by  $\Delta(\text{core})$  in Table 4, which is due to the fact that in HCO the  $7a'$  orbital is singly occupied and therefore not fully available for excitations (“truncation of the correlation space”, compare [22]). Table 4 shows that  $\Delta(\text{core})$  is remarkably basis set independent although the total core correlation energies of  $\text{HCO}^+$  and HCO increase rapidly with increasing basis size.  $\Delta(\text{core})$  has to be considered as a non-dynamic or structural correlation [23]. The second contribution to  $\Delta E_{\text{corr}}$ , the “odd electron” correlation, on the other hand, is purely dynamic and depends very strongly on the basis; there is a gain of almost a factor of two between DZ and  $TZ + 2d1f2p$ .

In earlier analyses of correlation effects (e.g. for the  $^1B_1$  Rydberg series in  $\text{H}_2\text{O}$  [21]) we have always found that the odd electron correlation energy is larger (in absolute value) than the loss of core correlation energy, such that the total correlation energy in the neutral system is larger (in absolute value) than in the ion. For HCO it is just the opposite: Table 4 shows that  $\Delta(\text{core})$  is larger than

**Table 4.** Decomposition of  $\Delta E_{\text{corr}}$  for  $\text{IP}_v$  in CEPA(SD) approximation<sup>a</sup>

Basis	HCO <sup>+</sup>	HCO		$\Delta(\text{core})^d$	$ \Delta E_{\text{corr}} $
	core <sup>b</sup>	core <sup>b</sup>	$7a'^c$		
DZ	250.76	190.12	28.04	60.64	32.60
DZ + <i>dp</i>	332.33	269.79	46.48	62.55	16.07
TZ	264.24	203.60	30.19	60.64	30.45
TZ + <i>d<sub>s</sub>p</i>	302.65	239.68	40.56	62.97	22.42
TZ + <i>dp</i>	347.62	284.70	47.93	62.92	15.00
TZ + <i>rdp</i>	348.23	286.02	47.85	62.22	14.36
TZ + 2 <i>d1p</i>	361.68	300.76	51.61	60.92	9.31
TZ + 2 <i>d1f2p</i>	387.50	326.33	54.64	61.17	6.53
ext.	270.20	210.19	31.16	60.01	28.85
ext. + <i>dp</i>	355.11	292.48	48.54	62.63	14.09

<sup>a</sup> All entries negative; in mH (compare Table 3).

<sup>b</sup> Correlation among orbitals 3 to 7, i.e.  $3a'$  to  $1a''$ .

<sup>c</sup> Correlation between  $7a'$  and the core orbitals  $3a'$  to  $1a''$ .

<sup>d</sup> Difference in the "core" correlation energies of HCO<sup>+</sup> and HCO.

the  $7a'$  correlation energy for all basis sets used, but the difference of the two quantities, i.e.  $\Delta E_{\text{corr}}$ , decreases with increasing basis size. A detailed analysis of the various pair correlation energies reveals that the main contribution to  $\Delta(\text{core})$  stems from the  $6a'^2 \rightarrow 7a'^2$  double excitation in HCO<sup>+</sup>, i.e. from excitation from the bonding in-plane  $\pi$ -orbital into the corresponding low-lying antibonding  $\pi^*$ -orbital. Since the two valence orbitals  $6a'$  and  $7a'$  are described reasonably well with the smaller basis sets, the basis set independence of  $\Delta(\text{core})$  is not surprising.

The sum of the atomic valence shell correlation energies for C(<sup>3</sup>*P*) and O(<sup>3</sup>*P*) as calculated with our TZ+2*d1f2p* basis (0.260 a.u., CEPA(SD)) accounts for about 88% of the estimated atomic valence shell correlation energies [24]. If we assume that the TZ + 2*d1f2p* basis will also account for 88% of the  $7a'$  correlation energy in HCO we arrive at an estimate of  $-62 \cdot 10^{-3}$  a.u. for its basis set limit. Together with  $\Delta(\text{core}) = 61 \cdot 10^{-3}$  a.u. this leads to a very small positive value for  $\Delta E_{\text{corr}}$ , indicating that we have underestimated the influence of the basis in our extrapolations in the Tables 2 and 3.

A further decomposition of the correlation energy into external, semi-internal, spin-polarization and internal contributions [25, 26] does not lead to a more thorough understanding and is omitted here.

Sometimes the following argument is used in order to explain why pure *ab initio* methods are not very successful in producing reliable results for energy differences such as e.g. ionization potentials: If the basis set used in a calculation is only capable for accounting for say 70% of the total correlation energy, then one can only expect to obtain about 70% for  $\Delta E_{\text{corr}}$ . The present study as well as a previous analysis [25] shows that the situation is often more complex: There

might be certain contributions to  $\Delta E_{\text{corr}}$  which are obtained nearly completely, or even overestimated with a rather small basis set, while others, e.g. the pure dynamic contributions, converge very slowly with increasing basis size. In general, it needs a detailed analysis of the different contributions before one can try to extrapolate to the infinite basis. In our example one would have been completely misled if one had performed just one single calculation with the TZ +  $dp$  basis, which yields about 70% of the valence shell correlation energy. One would have obtained  $\Delta E_{\text{corr}} = -15 \cdot 10^{-3}$  a.u. on CEPA(SD) level (Tables 3, 4) and the extrapolation to 100% (= infinite basis) would have led to  $\Delta E_{\text{corr}} = -21 \cdot 10^{-3}$  a.u.

## 5. Conclusions

Though we were not able to confirm the surprising result of Dyke et al. [5] that electron correlation reduces the  $\Delta\text{SCF}$  value for the first vertical IP of HCO, this molecule has the unusual property that the correlation contribution to  $\text{IP}_v$  is very small. The reason for this is that the correlation between the core and the unpaired electron in HCO is nearly fully compensated by a loss in "core" correlation energy since in HCO the  $7a'$  orbital is singly occupied and only partially available for excitation. Such a loss can be observed in many systems, in HCO it is extremely large because excitations from the bonding in-plane C–O– $\pi$ -orbital ( $6a'$ ) into the corresponding low-lying antibonding  $\pi^*$ -orbital ( $7a'$ ) have large contributions to the total correlation energy of  $\text{HCO}^+$ .

In order to describe the correlation contributions correctly, it is compulsory to use large basis sets. While the basis saturation on  $\Delta\text{SCF}$  level is obtained easily—within an uncertainty of about 0.02 eV—and the loss of core correlation energy is nearly independent of the basis size, the purely dynamic correlation between the odd electron and the core converges extremely slowly with increasing basis size; in particular  $d$ ,  $f$  and higher angular terms play an important role. Our best basis set of TZ +  $2d1f2p$  quality misses the "odd-electron" correlation energy by at least 0.007 a.u. = 0.19 eV. Errors inherent in the CEPA scheme, pair natural orbital determination, neglect of relativistic corrections etc. seem to be of less importance.

We have tried several basis set extrapolations which agree reasonably well with each other and result in  $\text{IP}_v = 9.26$  eV,  $\text{IP}_a = 8.05$  eV. Both values are 0.12 eV lower than the respective "experimental electronic" IPs [5].

A similar study of the basis set problem for the calculation of the electron affinity of methylene has been published recently by Feller et al. [27]. The error of their best calculation is of the same order as our TZ +  $2d1f2p$  error, their conclusion "the systematic nature of the errors in the theoretical calculations of electron affinities makes it unlikely that small increases in basis set or CI will significantly affect the results reported here" applies to our calculation of IPs as well.

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