Proton Affinity and Enthalpy of Formation of Formaldehyde

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ABSTRACT: The proton affinity and the enthalpy of formation of the prototypical carbonyl, formaldehyde, have been determined by the first-principles composite focal-point analysis (FPA) approach. The electronic structure computations employed the all-electron coupled-cluster method with up to single, double, triple, quadruple, and even pentuple excitations. In these computations the aug-cc-p(C)V*X*Z [X = 2(D), 3(T), 4(Q), 5, and 6] correlation-consistent Gaussian basis sets for C and O were used in conjunction with the corresponding aug-cc-pV*X*Z (X = 2–6) sets for H. The basis set limit values have been confirmed via explicitly correlated computations. Our FPA study supersedes previous computational work for the proton affinity and to some extent the enthalpy of formation of formaldehyde by accounting for (a) electron correlation beyond the "gold standard" CCSD(T) level; (b) the non-additivity of core electron correlation effects; (c) scalar relativity; (d) diagonal Born–Oppenheimer corrections computed at a correlated level; (e) anharmonicity of zero-point vibrational energies, based on global potential energy surfaces and variational vibrational computations; and (f) thermal corrections to enthalpies by direct summation over rovibrational energy levels. Our final proton affinities at 298.15 (0.0) K are $\Delta_{pa}H^{o}$ (H_2CO) = 711.02 (704.98) ± 0.39 kJ mol^{-1}. Our final enthalpies of formation at 298.15 (0.0) K are $\Delta_{f}H^{o}$ (H_2CO) = −109.23 (−105.42) ± 0.33 kJ mol^{-1}. The latter values are based on the enthalpy of the $H_2 + CO \rightarrow H_2CO$ reaction but supported by two further reaction schemes, $H_2O + C \rightarrow H_2CO$ and $2H + C + O \rightarrow H_2CO$. These values, especially $\Delta_{pa}H^{o}$ (H_2CO), have better accuracy and considerably lower uncertainty than the best previous recommendations and thus should be employed in future studies. © 2009 Wiley Periodicals, Inc. Int J Quantum Chem 109: 2393–2409, 2009

Key words: proton affinity; enthalpy of formation; formaldehyde; focal-point analysis; first-principles thermochemistry

Introduction

Though it is not the only factor, it is well established [1–17] that proton migration is crucial in inducing fragmentation in tandem mass spectrometry (MS/MS) experiments. The ease or difficulty of proton migration depends on the proton affinity (PA) [or the related gas-phase basicity (GB)] values of the protonation sites. Therefore, detailed experimental and/or theoretical investigation of the PA scale has special relevance for MS/MS experiments. A widely used experimental method to determine GBs (or PAs) by mass spectrometry is the kinetic method of Cooks [18]. It is based on the measurements of relative intensities of the B_1H^+ and B_2H^+ fragment ions generated by the dissociation of the proton-bound dimer $[B_1 \ldots H \ldots B_2]^+$. The kinetic method was used to determine GBs and PAs for many species, including amino acids [19–21] and amino acid dimers [22]. Harrison [23] gave a critical evaluation of these and other related studies.

The most important practical use of proton mobility is in proteomics studies, i.e., during the identification of biologically important proteins and their posttranslational modifications. This identification is based on tandem MS/MS fragmentation of protonated peptides. The ease of fragmentation, i.e., the relative abundance of sequence specific fragments depends on the amino acid composition of the peptide: peptides containing basic amino acids, such as arginine (R) and lysine (K) fragment less efficiently than those without these amino acid components. There are several detailed and systematic studies of peptide fragmentation mechanisms [1–17], the main conclusions of which have been summarized in the so-called mobile proton model [15–17] and the more recent pathways in competition (PIC) model [5]. According to the mobile proton model, the proton(s) added to a peptide during ionization will migrate to various sites upon ion activation. This migration then leads to a heterogeneous population of protonated forms. Some of these forms are easy to fragment ("fragmenting" structures) but some others, in which the proton is held more strongly at a higher PA site, will not fragment easily. In other words, proton migration and formation of a heterogeneous protonated peptide ion population is a prerequisite for peptide fragmentation. Of course, detailed energetic and kinetic characterization of the main fragmentation pathways (i.e., the application of the PIC model) is necessary to describe the relative fragment ion abundances. Besides experimental methods, such as the recently published combination of sustained off-resonance irradiation hydrogen/deuterium exchange (SORI-HDX) experiments [24] and infrared ion spectroscopy [25, 26], theoretical methods are of particular relevance in this field as it is well reflected by the recent work of one of István Mayer's successful former students, Béla Paizs [5, 25, 26].

As this article is dedicated to István Mayer, it is inevitable to mention here Mayer's direct and indirect contributions to the development of the mobile proton model. The recognition that different forms of protonated peptides can be correlated to their fragmentation efficiency was based on simple bond-order calculations using a population analysis method developed by Mayer [27]. The most important findings of the studies performed by one of the authors (ÁS) in collaboration with Mayer and Wysocki and detailed in [1, 2] are as follows: (a) the amide bond orders for the forms protonated on the amide nitrogen are significantly smaller, by about 30%, than for the corresponding neutral species; and (b) the amide bond orders in the forms protonated on the amide oxygen are significantly larger, again by about 30%, than in the neutrals. These computed results were crucial to realize that even though the forms protonated on the amide nitrogen are higher in energy (they have lower PAs) than the corresponding forms protonated on the amide oxygen, the amide nitrogen protonated forms are more likely to fragment at the amide bond than the other protonated forms. This finding was later found to be in excellent agreement with more detailed potential energy surface computations at higher levels of electronic structure theory by Paizs et al. [5, 25, 26] and Komáromi et al. [3].

Several studies [28–37], including elaborate experiments, sophisticated first-principles quantum chemical computations, and critical reviews and compilations, have been advanced which attempted to fix the absolute proton affinity scale of organic compounds. To accomplish this goal, the PAs of molecules at both the high and low end of the scale must be pinpointed. In a recent study [35], performed by two of the authors of this article (GC and AGC) and their coworkers, this anchoring was achieved by state-of-the-art quantum chemical computations on the PAs of ammonia (NH_3) and carbon monoxide (CO) as they have extremely different proton affinities at the low (CO) and the high (NH_3) ends of the absolute PA scale. The best 298.15 K PAs resulting from that study are $\Delta_{pa}H^o_{298}(NH_3) = 852.6 \pm 0.3$ kJ mol^{-1} and $\Delta_{pa}H^o_{298}(CO) = 592.4 \pm 0.2$ kJ mol^{-1} [35].

In this study, the PA of formaldehyde, $H_2C{=}O$, the prototypical carbonyl, has been studied at similarly sophisticated levels as those used for CO and NH_3. The PA of neutral H_2CO is defined as the negative of the enthalpy change for the isogyric reaction $H_2CO + H^+ \rightarrow H_2COH^+$. The PA at 0 K can thus be obtained by performing quantum chemical computations for the electronic energies and zero-point vibrational energies of H_2CO and H_2COH^+. Because results of the sophisticated and thus expensive quantum chemical computations performed for H_2CO can directly be used to determine its enthalpy of formation (EF) through simple elementary reactions, this study also examines $\Delta_f H^o_{298}(H_2CO)$ in detail.

The present focal-point analysis (FPA) [38, 39] study pushes the ab initio treatment of the proton affinity (and enthalpy of formation) of H_2CO to new heights by means of the following advances: (a) electron correlation beyond the "gold standard" CCSD(T) level is taken into account by performing coupled cluster computations complete through quadruple excitations; (b) FPA limits are determined with all electrons correlated, avoiding any additivity assumptions regarding valence and core correlation; (c) the basis set limits at correlated levels of electronic structure theory are determined not only through well-established extrapolation schemes but also by highly accurate explicitly-correlated CCSD(T)-F12 computations [40]; (d) relativistic shifts are evaluated by first-order perturbation theory applied to the mass-velocity and one-electron Darwin terms (MVD1) [41, 42] and by the Douglas–Kroll–Hess approach [43]; (e) the electronic structure computations go beyond the clamped nucleus assumption by appending diagonal Born-Oppenheimer corrections (DBOC) [44–47] to them; (f) anharmonic zero-point vibrational energies (ZPVEs) have been determined by performing full-dimensional variational vibrational motion computations using global ground-state potential energy surfaces (PES); and (g) the enthalpy increments needed to convert the 0 K computational results to finite temperatures, in the present case 298.15 K, have been obtained by explicitly summing over the rotational terms and the variationally computed vibrational energy levels within standard statistical mechanical expressions.

The results of selected previous attempts to determine the PA [33, 36, 48–61] and EF [62–75] of H_2CO are summarized in Tables I and II, respec-

TABLE I

Selected literature data for the proton affinity of H_2CO (in kJ mol^{-1}).

$\Delta_{pa} H^{o}_{298}$ ($\Delta_{pa}H^{o}_{0}$)	Authors and references	Comments
Measurements		
673 ± 13	Harrison et al. [49]	(1a)
703 ± 4	Haney and Franklin [51]	(1b)
724 ± 8	Freeman et al. [52]	(1c)
712.9 ± 1.0	Traeger and Holmes [55]	(1d)
Ab initio computations		
711.8 (705.8)	Smith and Radom [34]	(1e)
712.4	Hammerum [60]	(1f)
713.0 (709.4)	Seo et al. [54]	(1g)
Reviews and evaluations		
718	Lias et al. [36]	(1h)
711.3	Hunter and Lias [33]	

(1a) Estimated value based on a measured appearance potential for H_2COH^+ (736 ± 13 kJ mol^{-1}) and enthalpies of formation of formaldehyde (−116 kJ mol^{-1}) and of H^+ (1,527 kJ mol^{-1}). Note that the latter two values are substantially different from the best available values of today.

(1b) Derived based on photoionization measurements on lower aliphatic alcohols reported in Refaey, K. M. A.; Chupka, W. A. J Chem Phys 1968, 48, 5205.

(1c) This value was reported as a relative proton affinity based on flowing afterglow experiments at 300 K in both the forward and reverse directions of the reactions $H_2COH^+ + H_2S \leftrightarrow H_3S^+ + H_2CO$ and $H_2COH^+ + HCN \leftrightarrow H_2CN^+ + H_2CO$.

(1d) This value is based on threshold photoionization mass spectrometry measurements and the determination of the enthalpy of formation of H_2COH^+ (708.5 ± 0.8 kJ mol^{-1}). The idea is that the values of $\Delta_f H^{o}_{298}$ (M) are known for many (small) molecules, as well as $\Delta_f H^{o}_{298}$ (H^+) = 1,530 kJ mol^{-1}. From these values, experimental PAs can be calculated. Note that this PA value critically depends on EF(H_2CO), which was assumed to be −108.6 ± 0.8 kJ mol^{-1} [71].

(1e) Calculated using the G2 model chemistry. Further similar values, 712. 8 and 712.2 kJ mol^{-1}, obtained at the G2(MP2) and G2(MP2,SVP) levels, respectively, by the same authors are reported in Ref. [56].

(1f) Calculated using the G3 model chemistry from total energies and calculated integrated heat capacities. The same report also lists G2(MP2) and CBS-Q values.

(1g) Calculated at the MC-QCISD//ML level, see Table IV of Ref. [54]. Note the seemingly incorrect thermal correction.

(1h) In their extensive compilation of gas-phase PA and GB values, Lias et al. [36] adopted the value of 718 kJ mol^{-1}. This value was based on a high PA value of water, 697 ± 8 kJ mol^{-1}. If a lower PA value of water is adopted, it would lower the recommended PA(H_2CO) value of Lias et al. As pointed out by Traeger and Holmes [55], another accepted PA(H_2CO) value, 690.8 ± 2.9 kJ mol^{-1} leads to a value of about 712 kJ mol^{-1}.

tively. The most recent PA values are in reasonably good agreement though the drift from the early measured and evaluated values is quite notable. There are both low- and high-end recommended values for the EF of H_2CO. The high-end value of −108.6 ± 0.5 kJ mol^{-1} has been measured by Fletcher and Pilcher [62] and was recommended in several compilations of EF values. The low-end value of about −116 kJ mol^{-1} dates back to 1925 [65] but was recommended by JANAF even in 1998 [73]. The usually more dependent compilation of enthalpies of formation due to Gurvich and coworkers recommended the substantially different value of −108.70 ± 0.50 kJ mol^{-1}. The best previous ab initio value, employing the composite W4 approach [76], is −105.34 kJ mol^{-1} at 0 K, corresponding to a total atomization energy (TAE) of 1495.82 kJ mol^{-1}, also at 0 K. Note that this TAE value is very close to the best Active Thermochemical Tables (ATcT) [77] estimate of the same quantity, 1495.49 ± 0.25 kJ mol^{-1}. Converting the W4 enthalpy of formation value to 298.15 K with a factor given in Ref. [78], −3.84 kJ mol^{-1}, results in $\Delta_f H^{o}_{298}(H_2CO) = -109.18$ kJ mol^{-1}.

Despite the large amount of existing information for the PA and EF of formaldehyde, the attendant uncertainty of PA is still considerably larger than what can be achieved from state-of-the-art computations on molecules of this size [78–92]. For small molecules and radicals (at present up to 5–6 "heavy" atoms), first-principles computations of thermochemical quantities are often more accurate than experimental measurements; frequently, the uncertainties of the best computed values can only be surpassed by comprehensively incorporating both empirical and theoretical data in schemes such

TABLE II

Selected literature data for the enthalpy of formation of H_2CO at 298.15 K (in kJ mol^{-1}).

$\Delta_f H^\circ_{298}$ ($\Delta_f H^\circ_0$)	Authors and references	Comments
Measurements		
−115.90	Wartenberg and Learner-Steinberg [65]	(2a)
−104.60	Delepine and Badoche [63]	
−108.57 ± 0.46	Fletcher and Pilcher [62]	(2b)
Ab initio computations		
−116.73 (−112.97)	Curtiss et al. [66]	(2c)
−111.29	Montgomery et al. [67]	(2d)
−109.18 (−105.34)	Martin et al. [76]	(2e)
−109.79 ± 1.84	da Silva et al. [68]	(2f)
−108.7(−104.8)	Nagy [140]	(2g)
Reviews and evaluations		
−117.15 ± 6.28	Stull et al. [69]	(2h)
−108.78	Domalski et al. [74]	
−108.57	Chao [72]	
−108.57 ± 0.46	Baulch et al. [69]	
−108.57 ± 0.50	Pedley et al. [71]	
−108.70 (−104.86) ± 0.50	Gurvich et al. [64]	
−115.90 ± 6.28	Chase [73]	
−108.53	Marsh et al. [75]	

(2a) Determined by combustion measurements as −27.7 kcal mol^{-1}.

(2b) Measured in the gaseous state at 298 K and 1 atm pressure using a flame calorimeter.

(2c) The enthalpy of formation of formaldehyde at 0 and 298 K has been determined by the well-known G2 model chemistry. The reported values were −27.0 and −27.9 kcal mol^{-1} at 0 and 298 K, respectively.

(2d) Determined using the CBS-4M, CBS-QB3, G3(MP2), and G3 model chemistries as −26.8, −27.0, −26.6, and −26.6 kcal mol^{-1}, respectively.

(2e) The computed 0 K value of −105.34 kJ mol^{-1}, based on a total atomization energy of 1495.82 kJ mol^{-1} and the enthalpies of formation of H, C, and O of 216.03, 711.58, and 246.84, respectively (as used in this study), was converted to the 298.15 K value using the correction factor of −3.84 kJ mol^{-1} taken from Ref. [78].

(2f) Determined using six model chemistries: CBS-Q, CBS-Q//B3, CBS-APNO, G2, G3, and G3B3. The reported values were −25.90 ± 1.17, −26.24 ± 0.44 and −26.82 ± 0.94 kcal mol^{-1} via an enthalpy of reaction, an isodesmic, and an atomization scheme, respectively. Only the middle value with the lowest uncertainty estimate is reported in the table.

(2g) Determined using the HEAT model chemistry [85]. The thermal correction was obtained within the rigid rotor – harmonic oscillator approximation using AE-CCSD(T)/cc-pVQZ data.

(2h) Calculated −28.44 kcal mol^{-1} from $\Delta_r H_{298} = -19.637$ kcal mol^{-1} of the reaction HCHO(g) + H_2(g) = CH_3OH(g) [Newton, R. H., Dodge, B. F. J Am Chem Soc 1933, 55, 4747] and the corresponding $\Delta_f H^\circ_{298}$ (CH_3OH) = −48.080 kcal mol^{-1}. Based on this and other available information to the authors, they selected the enthalpy of formation of formaldehyde to be −28.0 ± 1.5 kcal mol^{-1}.

as the ATcT approach [77]. Previous computations of thermochemical quantities [35, 78–92] employing variants of the focal-point analysis (FPA) approach, clearly prove the effectiveness of the sophisticated first-principles methods employed in this study.

Computational Methods

The aug-cc-p(C)V*X*Z [*X* = 2(D), 3(T), 4(Q), 5, and 6] families of correlation-consistent, atom-centered Gaussian basis sets [93–96] were employed in this study for the traditional electronic structure computations. The orbital contraction schemes of these basis sets range from (11*s*6*p*2*d*) → [5*s*4*p*2*d*] to (22*s*16*p*10*d*8*f*6*g*4*h*2*i*) → [13*s*12*p*10*d*8*f*6*g*4*h*2*i*] for C and O, and from (5*s*2*p*) → [3*s*2*p*] to (11*s*6*p*5*d*4*f*3*g*2*h*) → [7*s*6*p*5*d*4*f*3*g*2*h*] for H. These atomic-orbital basis sets give superior performance in approaching the complete basis set (CBS) limit in a systematic fashion during traditional electronic structure computations. When aug-cc-pCV*X*Z sets were used to effectuate the correlation of core electrons for C and O, the corresponding aug-cc-pV*X*Z functions were utilized for H.

This study also utilized special basis sets designed for F12 electronic structure computations. Instead of the linear r_{12} term in the original CCSD(T)-R12 technique [97], in CCSD(T)-F12 a Slater-type geminal (STG) $\exp(-\gamma r_{12})$ is used as the correlation factor [40]. Similarly to Ref. [40], γ has been fixed here to 1.0, which is a compromise value resulting from second-order F12. The current implementation of CCSD(T)-F12 theory requires that the basis sets employed are fairly saturated at the level of $3L_{\text{occ}}$, where L_{occ} is the highest angular momentum function involved in the occupied orbitals. Hence, from the aforementioned correlation-consistent sets we restricted ourselves to aug-cc-pCV*X*Z with cardinal numbers $X = 5$ and 6. Furthermore, the reliability of these CCSD(T)-F12 computations has been checked by computations using fully uncontracted R12-suited basis sets, which can be denoted as (9*s*6*p*4*d*3*f*) for hydrogen [98] and (19*s*14*p*8*d*6*f*4*g*3*h*) [99] for nonhydrogen atoms. For H, the 9*s* set is identical to that of the aug-cc-pV5Z basis [93], whereas for the nonhydrogen atoms the *sp* sets were taken from the Hartree–Fock limit sets of Partridge [100]. With these extended basis sets the inaccuracy introduced by a not fully optimized choice for the γ exponent is very small. Matrix elements within CCSD(T)-F12 were evaluated by using variant "C" of the standard approximation [40, 101].

Reference electronic wave functions for the closed-shell species of this study, H_2CO, H_2COH^+, H_2O, H_2, and CO, were determined by the single-configuration restricted Hartree–Fock (RHF) method [102]. Electron correlation was accounted for by the coupled-cluster (CC) method [103, 104] including all single and double (CCSD), triple (CCSDT), and quadruple (CCSDTQ) excitations [105]. The CCSD(T) [106] and CCSDT(Q) [107, 108] methods, which include perturbative (T) and (Q) terms for connected triple and quadruple excitations, respectively, were also used extensively. The effect of pentuply substituted determinants has been evaluated at the CCSDTQ(P) level [107]. Because of the high computational cost of this approach, the aug-cc-pVDZ basis set and the frozen-core approximation were employed in the CCSDTQ(P) computations. All electrons were included, unless otherwise noted, in the active space for all the other correlation energy computations. For the open-shell species of this study (atoms H, C, and O), the energies reported result from calculations based on unrestricted Hartree–Fock (UHF) references. Using restricted open-shell HF (ROHF), the HF energies will, of course, differ, but as soon as one goes to the CCSD level (and beyond), as done here, the differences between UHF- and ROHF-based energies and the spin contamination introduced by the UHF reference become irrelevant.

In the spirit of the FPA approach [38, 39], the aug-cc-pCV*X*Z sequences of electronic energies were extrapolated to determine the complete basis set (CBS) limits. For extrapolation of the Hartree–Fock energies, the following two-parameter [109–111] exponential function of the cardinal number *X* was used,

$$E_X^{\text{HF}} = E_{\text{CBS}}^{\text{HF}} + a(X+1)e^{-9\sqrt{X}}. \tag{1}$$

The results are reported in Tables III and IV as the CBS HF proton affinity and reaction enthalpy values, respectively. The CCSD and CCSD(T) electron correlation energies ($\varepsilon_X \equiv E_X^{\text{CC}} - E_X^{\text{HF}}$) were extrapolated using a two-parameter polynomial formula [112]

$$\varepsilon_X = \varepsilon_{\text{CBS}} + bX^{-3}. \tag{2}$$

The program packages MAB-ACESII [113], MRCC (interfaced to ACESII) [114], and MOLPRO [115] were used for the "conventional" electronic structure computations. Analytic gradient techniques [116–118], as implemented in MAB-ACESII, were utilized to obtain optimum geometric structures at the all-electron (AE) CCSD(T)/aug-cc-pCVQZ level. These structures were adopted for all electronic structure computations involved in the FPA analyses. A modified version of the program package DIRCCR12-OS [119] with STG integral routines provided by Ten-no [120] was used for the explicitly correlated CCSD-F12 and CCSD(T)-F12 computations.

The DBOC corrections at the HF level were computed with MAB-ACESII and the aug-cc-pVTZ basis. The correlated-level frozen-core (FC) CISD/aug-cc-pVDZ DBOC computations utilized the formalism of Ref. [47] as implemented in the PSI3 electronic structure package [121]. Relativistic effects were evaluated by first-order perturbation theory applied to the mass-velocity and one-electron Darwin terms (MVD1) [41] as implemented in MAB-ACESII, as well as with the Douglas–Kroll–Hess (DKH) approach [43] as part of MOLPRO. For this purpose, AE-CCSD(T)/aug-cc-pCVTZ wave functions were employed.

TABLE III

Focal-point analysis of the all-electron non-relativistic Born–Oppenheimer proton affinity (ΔE_e, kJ mol^{-1}) of H_2CO at 0 K.[a]

	ΔE_e(RHF)	δ[CCSD]	δ[CCSD(T)]	δ[CCSDT]	δ[CCSDT(Q)]	δ[CCSDTQ][d]	δ[CCSDTQ(P)][d]	ΔE_e (final)
Traditional								
aug-cc-pCVDZ	770.70	–25.48	–4.45	+0.19	–0.87	+0.11	–0.10	740.10
aug-cc-pCVTZ	775.91	–26.81	–6.04	+0.44	–0.90[c]	[+0.11]	[–0.10]	[742.61]
aug-cc-pCVQZ	776.62	–27.39	–6.38	[+0.44]	[–0.90]	[+0.11]	[–0.10]	[742.40]
aug-cc-pCV5Z	776.83	–27.80	–6.50	[+0.44]	[–0.90]	[+0.11]	[–0.10]	[742.08]
aug-cc-pCV6Z	776.86	–28.06	–6.55	[+0.44]	[–0.90]	[+0.11]	[–0.10]	[741.80]
CBS[b]	[776.87]	[–28.40]	[–6.62]	[+0.44]	[–0.90]	[+0.11]	[–0.10]	[741.40]
Explicitly correlated								
aug-cc-pCV5Z	776.83	–28.52	–6.45					
aug-cc-pCV6Z	776.86	–28.48	–6.52					
R12-basis	776.81	–28.45	–6.51					

[a] Based on AE-CCSD(T)/aug-cc-pCVQZ reference structures. For the all-electron coupled cluster computations, the symbol δ denotes the increments, in ΔE_e, with respect to the preceding level of theory. Brackets within the body of the table signify increments obtained from basis set extrapolations [in case of CBS HF, CCSD, and CCSD(T)] or additivity approximations based on traditional CC total energies. The explicitly correlated results refer to the F12 formalism (see text for details).

[b] The complete basis set RHF, CCSD, and CCSD(T) entries were obtained from aug-cc-pCV(5,6)Z energies using the two-parameter extrapolation formulas given in Eqs. (1) and (2).

[c] The computed increment is based on frozen-core computations using the aug-cc-pVTZ basis set. The difference between the frozen-core and all-electron CCSDT(Q) increments using the aug-cc-p(C) VDZ bases is less than 0.01 kJ mol^{-1}.

[d] The computed increments are based on frozen-core computations employing the aug-cc-pVDZ basis set.

The global PESs of both H_2CO and H_2COH^+ were obtained as a fit to ab initio energies computed at the FC-CCSD(T)/aug-cc-pVTZ level of theory with the MOLPRO program package. The ROHF-RCCSD(T) formalism was employed for the open-shell fragment species. The interest of this study is limited to the region near the global minimum; nevertheless, ab initio data for several fragmentation channels was also included in the fit. For both surfaces ab initio data points were weighted in the least-squares procedure using weight $w = E_0/(E + E_0)$, where E is the energy relative to the global minimum and E_0 is a parameter. In this study, as our interest is in the region near the global minimum, a rather small $E_0 = 0.02\ E_h$ value was utilized. The PESs were fitted using a polynomial basis in Morse-like variables of internuclear distances, which is invariant under permutation of the H atoms. All terms up to degree 6 were included in the least-squares fit. The total number of free coefficients is 1,601 and 1,618 for the PESs of H_2CO and H_2COH^+, respectively.

For the H_2CO surface the database contains 35,573 configurations in the complex region. Fragment data were included for the channels H + HCO (5,000 configurations), H_2 + CO (3,000 configurations), CH + OH (2,000 configurations), H_2O + C(singlet) (1,000 configurations), and CH_2(singlet) + O(singlet) (1,000 configurations). The high-energy fragmentation channels carry low weight in the fit, they are included only to prevent pathological behavior of the fitted surface for those channels. The fragment energies were computed using the same FC-RCCSD(T)/aug-cc-pVTZ level. The exceptions are H_2, for which FCI was used and H, for which the exact Born–Oppenheimer value, $-0.5\ E_h$ was employed. The root mean square (rms) fitting error in the vicinity of the global minimum can be characterized as follows: for configurations in the complex region that have energy E (relative to the global minimum) in the range 0–4,390 cm^{-1} and the rms error is 41 cm^{-1}. For configurations in the complex region in the range 4,390–8,780 cm^{-1} it is 79 cm^{-1}, and for those in the range 8,780–21,947 cm^{-1} it is 201 cm^{-1}. There are 497, 1,047, and 5,288 configurations respectively in those three ranges.

For the H_2COH^+ surface the database is smaller, containing 6,014 configurations in the complex region. Fragment data were included for the channels H + H_2CO^+ (1,000 configurations) and H_2 + HCO^+ (1,000 configurations). For configurations in the complex region that have energy E in the ranges 0–4,390, 4,390–8,780, and 8,780–21,947 cm^{-1} the

TABLE IV

Focal-point analysis of the all-electron non-relativistic Born−Oppenheimer reaction enthalpies (ΔE_e, kJ mol^{-1}) forming H_2CO at 0 K using three reaction schemes.[a]

H_2+CO → H_2CO	ΔE_e(RHF)	δ[CCSD]	δ[CCSD(T)]	δ[CCSDT]	δ[CCSDT(Q)]	δ[CCSDTQ]	δ[CCSDTQ(P)][b]	ΔE_e(final)
Traditional								
aug-cc-pCVDZ	–4.88	–13.51	+0.97	–0.11	+0.25	–0.01	–0.01	–17.30
aug-cc-pCVTZ	1.48	–23.42	+0.49	–0.06	+0.28	[–0.01]	[–0.01]	[–21.25]
aug-cc-pCVQZ	2.69	–25.46	+0.35	[–0.06]	[+0.28]	[–0.01]	[–0.01]	[–22.22]
aug-cc-pCV5Z	2.76	–25.67	+0.35	[–0.06]	[+0.28]	[–0.01]	[–0.01]	[–22.36]
aug-cc-pCV6Z	2.77	–25.78	+0.35	[–0.06]	[+0.28]	[–0.01]	[–0.01]	[–22.46]
CBS[c]	[2.77]	[–25.92]	[+0.35]	[–0.06]	[+0.28]	[–0.01]	[–0.01]	[–22.60]
Explicitly correlated								
aug-cc-pCV5Z	2.76	–25.79	+0.34					
aug-cc-pCV6Z	2.77	–25.87	+0.35					
R12-basis	2.77	–25.70	+0.39					
H_2O + C → H_2CO	ΔE_e(UHF)	δ[CCSD]	δ[CCSD(T)]	δ[CCSDT]	δ[CCSDT(Q)]	δ[CCSDTQ]	δ[CCSDTQ(P)][b]	ΔE_e(final)
Traditional								
aug-cc-pCVDZ	−410.66	−119.52	−14.94	+0.44	−1.42	+0.24	−0.09	−545.95
aug-cc-pCVTZ	−424.74	−135.50	−17.87	+1.10	−1.69	[+0.24]	[−0.09]	[−578.55]
aug-cc-pCVQZ	−425.78	−142.36	−18.61	[+1.10]	[−1.69]	[+0.24]	[−0.09]	[−587.19]
aug-cc-pCV5Z	−425.79	−144.89	−18.86	[+1.10]	[−1.69]	[+0.24]	[−0.09]	[−589.98]
aug-cc-pCV6Z	−425.78	−146.06	−18.95	[+1.10]	[−1.69]	[+0.24]	[−0.09]	[−591.23]
CBS[c]	[−425.77]	[−147.66]	[−19.08]	[+1.10]	[−1.69]	[+0.24]	[−0.09]	[−592.95]
Explicitly correlated								
aug-cc-pCV5Z	−425.79	–147.56	−18.76					
aug-cc-pCV6Z	−425.78	–147.54	−18.89					
R12-basis	−425.83	–147.57	−18.83					
2H + O + C → H_2CO	ΔE_e(UHF)	δ[CCSD]	δ[CCSD(T)]	δ[CCSDT]	δ[CCSDT(Q)]	δ[CCSDTQ]	δ[CCSDTQ(P)][b]	ΔE_e(final)
Traditional								
aug-cc-pCVDZ	−1057.28	−383.30	−24.21	+0.60	−2.60	+0.39	−0.10	−1466.50
aug-cc-pCVTZ	−1075.96	−426.46	−31.97	+1.89	−2.58	[+0.39]	[−0.10]	[−1534.79]
aug-cc-pCVQZ	−1078.07	−444.01	−33.43	[+1.89]	[−2.58]	[+0.39]	[−0.10]	[−1555.91]
aug-cc-pCV5Z	−1078.05	−449.66	−33.90	[+1.89]	[−2.58]	[+0.39]	[−0.10]	[−1562.01]
aug-cc-pCV6Z	−1078.05	−452.00	−34.08	[+1.89]	[−2.58]	[+0.39]	[−0.10]	[−1564.53]
CBS[c]	[−1078.05]	[−455.21]	[−34.31]	[+1.89]	[−2.58]	[+0.39]	[−0.10]	[−1567.97]
Explicitly correlated								
aug-cc-pCV5Z	−1078.05	–455.04	−33.74					
aug-cc-pCV6Z	−1078.05	–455.02	−33.98					
R12-basis	−1078.00	–455.15	−33.75					

[a] See footnote a of Table III.
[b] See footnote d of Table III.
[c] See footnote b of Table III.

rms errors are 58, 103, and 272 cm^{-1}, respectively. There are 318, 471, and 1,599 configurations, respectively, in these three ranges.

The variational vibrational computations were performed in full dimensions with the program Multimode (MM) [122] using the vibrational configuration interaction (VCI) method and allowing a maximum of five simultaneously excited modes in the basis. MM employs the Eckart–Watson Hamiltonian [123] of nonlinear molecules expressed in normal coordinates and the so-called n-mode representation (nMR) [124] of both the PES and the inverse of the effective moment of inertia tensor. The VCI computations employed 4MR; it provides low-lying vibrational levels within about wavenumber accuracy corresponding to a given PES (for more details, see [125]). The basis sets of 2,240 and 12,841 functions employed for H_2CO and H_2COH^+, respectively, provide converged ZPVEs (within 1 cm^{-1}).

TABLE V

Auxiliary corrections (DBOC, relativistic MVD1(DKH), and ZPVE) for the FPA approach and the resulting proton affinity (PA) and reaction enthalpy (RE, through the reaction H_2 + CO → H_2CO) corrections, all in kJ mol^{-1}.

	DBOC[a]			
	RHF	Corr. contrib.	Relativistic MVD1(DKH)[b]	ZPVE[c]
H_2CO	11.89	+0.23	–175.94 (–167.14)	69.21
H_2COH^+	12.02	+0.24	–175.80 (–167.01)	105.36
PA(H_2CO)	–0.13	–0.01	–0.14 (–0.13)	–36.15
H_2	1.21	+0.16	–0.025 (–0.025)	26.07
CO	10.50	+0.11	–176.66 (–167.83)	12.94
RE(H_2CO)	0.18	–0.04	+0.74 (+0.72)	+30.12[d]

[a] RHF = RHF/aug-cc-pVTZ//AE-CCSD(T)/aug-cc-pCVQZ computations. The correlation contributions to the DBOC corrections (Corr. contrib.) have been evaluated at the FC-CISD/aug-cc-pVDZ//AE-CCSD(T)/aug-cc-pCVQZ level.

[b] The AE-CCSD(T)/aug-cc-pCVTZ//CCSD(T)/aug-cc-pCVQZ level was used for both the MVD1 and DKH computations. The AE-CCSD(T)/aug-cc-pCVQZ//CCSD(T)/aug-cc-pCVQZ level DKH results for PA(H_2CO) and EF(H_2CO) are –0.12 and +0.72 kJ mol^{-1}, respectively.

[c] For H_2CO and H_2COH^+ accurate anharmonic ZPVEs were computed in this study based on harmonic ZPVEs obtained at the AE-CCSD(T)/aug-cc-pCVTZ level and anharmonic corrections based on a variational vibrational method. For H_2 and CO, variationally computed ZPVEs reported in the literature are taken.

[d] For this value, ZPVE(H_2CO) taken from the literature, 69.13 kJ mol^{-1} [143], was used and not the estimate computed in this study (see Section “Zero-point vibrational energies” for details).

TABLE VI

Zero-point vibrational energy (ZPVE) and all the fundamentals (in cm^{-1}) of H_2COH^+ computed variationally.

	ω^a	$\Delta\nu^b$	ν^c	Expt.[d]
ZPVE	8939	−132	8807	
$\nu_9(a'')$	1032	−44	988	[*993*]
$\nu_7(a')$	1117	−18	1099	[*1107*]
$\nu_8(a'')$	1238	−20	1218	
$\nu_6(a')$	1392	−48	1344	[*1357*]
$\nu_5(a')$	1482	−36	1446	[*1465*]
$\nu_4(a')$	1659	−40	1619	[*1621*]
$\nu_3(a')$	3107	−147	2960	
$\nu_2(a')$	3253	−138	3115	
$\nu_1(a')$	3597	−178	3419	3423

[a] *Ab initio* harmonic frequencies obtained at the AE-CCSD(T)/aug-cc-pCVTZ level of theory.

[b] Anharmonic corrections obtained as differences between the variationally computed vibrational energies and the harmonic values corresponding to the same fitted PES.

[c] Anharmonic vibrational energies obtained as $\omega + \Delta\nu$.

[d] The experimental OH stretching frequency of H_2COH^+ is taken from Ref. [146]. Note that the experimental (Expt.) wavenumbers reported in brackets and printed in italics correspond to the H_2COH radical (with data taken from Ref. [152]) and not to the H_2COH^+ cation.

Results and Discussion

The primary focal-point analyses of the PA and EF of H_2CO are presented in Tables III and IV, respectively. The auxiliary data for the DBOC, relativistic, and ZPVE corrections are given in Table V. Table VI lists the variationally computed fundamentals for H_2COH^+.

REFERENCE STRUCTURES

For all molecules, AE-CCSD(T)/aug-cc-pCVQZ equilibrium structures were used as reference geometries in our FPA computations. Simple expectation, measurements [126], and even early simple ab initio electronic structure computations [127–131] of enthalpies of formation showed that the most stable isomer of H_2COH^+ has the proton on O. Therefore, only this form was considered in the present study.

For H_2CO, of C_{2v} point-group symmetry, we employed [r_e(C—H), r_e(C═O), θ_e(H—C—H)] = (1.1007 Å, 1.2052 Å, 116.62°) as the reference structure. These geometric parameters are in excellent agreement with a possibly somewhat inaccurate experimental estimate [132] of the equilibrium structure [1.1005 (20) Å, 1.2033 (10) Å, 116.30 (25)°]. These empirical values are slightly different, though the same within the uncertainty limits, from the often quoted values of Yamada et al. [133], [1.099 (9) Å, 1.203 (3) Å, 116.5 (12)°], but have lower uncertainties. As expected [134], the close matching of experimental and computed equilibrium structures requires the correlation of all the electrons. All these values are also in nice agreement with the equilibrium structure estimate of Carter and Handy [135], [1.1003 (5) Å, 1.2031 (5) Å, 116.76 (5)°], who fitted the structure and the quadratic force field to observed vibrational-rotational data for H_2CO and D_2CO. See Table I of [135] for a compilation of equilibrium structure estimates of H_2CO not mentioned here. Finally, note must be made of the detailed structural study of polyatomics by Pawlowski et al. [136], where the following semiexperimental structure was determined for H_2CO: [r_e(C—H), r_e(C═O), θ_e(H—C—H)] = (1.1007 Å, 1.2047 Å, 116.74°), in outstanding agreement with the reference structure of this study.

The AE-CCSD(T)/aug-cc-pCVQZ equilibrium structural parameters for H_2COH^+, of C_s point-group symmetry, are as follows: $r_e(\mathrm{C—H})_{\mathrm{syn}}$ = 1.0876 Å, $r_e(\mathrm{C—H})_{\mathrm{anti}}$ = 1.0855 Å, r_e(O—H) = 0.9787 Å, r_e(CO) = 1.2461 Å, θ_e(H—C—H) = 122.77°, $\theta_e(\mathrm{H_{syn}—C—O})$ = 121.48°, and θ_e(C—O—H) = 115.23°. This structure agrees nicely with an empirical structure built upon measured moments of inertia of three isotopologues (H_2COH^+, $H_2{}^{13}COH^+$, and D_2COD^+) and a limited predicate least-squares refinement of the structural parameters [137].

NONRELATIVISTIC BORN–OPPENHEIMER PA AND EF

The present FPA analysis of the proton affinity of formaldehyde starts at the RHF/aug-cc-pCVDZ level, which yields 770.70 kJ mol^{-1} for the vibrationless PA of H_2CO. Enlarging the basis set to aug-cc-pCV6Z increases the Hartree-Fock PA by 6.16 kJ mol^{-1} or close to 1%. The difference between the aug-cc-pCV6Z and the CBS Hartree-Fock proton affinities is minuscule, less than 0.01 kJ mol^{-1}.

The electron correlation energies and the lowest-order FPA increments exhibit considerably slower basis set convergence. The aug-cc-pCV6Z and extrapolated (CBS) δ[CCSD] increments deviate by 0.34 kJ mol^{-1} for the PA of H_2CO. It is expected [38, 39] that the level of convergence of the CCSD increment determines largely the eventual uncertainty in the FPA value of $\Delta_{\mathrm{pa}}H_0^{\circ}(H_2CO)$. Consistent with the foundations of the FPA approach, all of the higher-order correlation increments, for which data are available, converge rapidly to their respective CBS limits; for example, the change in the δ[CCSD(T)] increment beyond aug-cc-pCV6Z is only 0.07 kJ mol^{-1}. Furthermore, both CCSD-F12 and CCSD(T)-F12 values with different extended basis sets vary only very slightly and suggest that the uncertainties in the CBS estimates of the corresponding increments are not larger than 0.05 kJ mol^{-1}.

The higher-order corrections are relatively small though significant at the level of precision seeked in this study. The final CBS estimates of the coupled-cluster correlation energy increments for $\Delta_{\mathrm{pa}}H_0^{\circ}(H_2CO)$ are −28.40, −6.18, and −0.79 kJ mol^{-1} for the full treatments of single and double (SD), triple (T), and quadruple (Q) excitations, in order. Note that due to the considerable cost of the required computations on H_2COH^+, the CCSDTQ and the CCSDTQ(P) computations utilized only the aug-cc-pVDZ basis set and the core electrons were kept frozen during these computations. The latter approximation should not introduce any noticeable error into the FPA analysis but the use of the sub-compact aug-cc-pVDZ basis is admittedly slightly restrictive. The total correlation contribution to the proton affinity is about 5%. From the sequences of CCSD, CCSDT, and CCSDTQ values, it appears that full inclusion of quintuple excitations would decrease $\Delta_{\mathrm{pa}}H_0^{\circ}(H_2CO)$ on the order of −0.1 kJ mol^{-1}. The actual frozen-core CCSDTQ(P)/aug-cc-pVDZ increment of −0.10 kJ mol^{-1} computed for the PA of H_2CO fully supports this expectation. Consequently, electron correlation effects beyond the gold standard CCSD(T) level give a PA correction of −0.45 kJ mol^{-1}, with a conservative uncertainty of 0.20 kJ mol^{-1}. In summary, the best PA estimate at the all-electron nonrelativistic complete basis set full configuration interaction (CBS FCI) limit is 741.40 ± 0.30 kJ mol^{-1}, where the uncertainty basically accounts for the lack of larger basis set higher-order treatments.

Next, let us discuss the enthalpy of formation of H_2CO, to be determined through three reactions, $H_2 + CO \rightarrow H_2CO$ (reaction 1), $H_2O + C \rightarrow H_2CO$ (reaction 2), and $2H + C + O \rightarrow H_2CO$ (reaction 3). Similarly to the PA, if one compares the extrapolated and the F12 numbers for the reaction enthalpy of reaction 1 involving only closed-shell species, one can observe extremely good agreement. This gives considerable confidence in the CBS CCSD(T) reaction enthalpy value of reaction 1. Although the extrapolated and the F12 numbers agree very well, it is worth mentioning that the computation combining the F12 technique with the aug-cc-pCV5Z basis set is significantly less expensive than the traditional aug-cc-pCV6Z CCSD(T) computation while yielding similar accuracy. The final computed reaction enthalpy of reaction 1, at the all-electron non-relativistic CBS FCI limit, with a conservative uncertainty estimate is −22.60 ± 0.20 kJ mol^{-1}.

The other two reactions studied contain open-shell species (atoms H, C, and O). In these cases the spin-orbit effects are relevant to achieve the target accuracy of this study. The required data considering first-order spin-orbit effects could be taken from [85].

In all three reaction schemes, an additional uncertainty is introduced via the basis set superposition error (BSSE), whose contribution for strong interactions is still questionable and computed unreliably within the well established counterpoise correction scheme. Nevertheless, as concluded in [138] for the atomization energies of small molecules, the BSSE is significantly reduced in explicitly correlated computations. This fact also plays an important role in the faster convergence of the pertinent results with CCSD-F12 toward the CBS limit. It is also notable that for reactions 2 and 3, the very nice agreement between traditional CCSD and CCSD(T) enthalpies of reaction and their F12 counterparts is lost. For reactions 2 and 3 the difference between the two CCSD values using the aug-cc-pCV6Z basis set is 1.48 and 3.02 kJ mol^{-1}, respectively. Fortunately, and this shows excellently the virtue of the polynomial basis set extrapolation included in the FPA analysis, these very sizable differences decrease drastically when the CBS and the F12 values are compared. The differences are almost acceptable, as they are 0.12 and 0.19 kJ mol^{-1} for reactions 2 and 3, respectively. Nevertheless, the large differences observed between the correlated aug-cc-pCV6Z and CBS results and the difference of the CBS and F12 results at the CCSD level suggest that it is better not to consider reactions 2 and 3 when computing the enthalpy of formation of formaldehyde.

To convert the computed reaction enthalpy of reaction 1 into an enthalpy of formation, one needs to know accurate enthalpies of formation for the species, except H_2CO, involved in this reaction. In this respect again reaction 1 stands out as one needs to know only the enthalpy of formation of CO for the conversion. This quantity has been well studied and an accurate ATcT value is available for it, −113.81 ± 0.17 kJ mol^{-1} [85]. The best estimates of the enthalpies of formation of H, O, and H_2O come also from the ATcT protocol [85] and they are 216.03 ± 0.00, 246.84 ± 0.00, and −238.92 ± 0.04 kJ mol^{-1}, respectively. The best estimate for the enthalpy of formation of the C atom has been the subject of some recent studies [139, 140], the best present estimate of this quantity appears to be 711.58 ± 0.10 kJ mol^{-1} [140].

In summary, our final CBS FCI values from Tables III and IV, with conservative uncertainty estimates, for the all-electron nonrelativistic contributions to the proton affinity and enthalpy of formation (through reaction 1) of H_2CO (without ZPVE) at 0 K are thus 741.40 ± 0.30 and −136.41 ± 0.26 kJ mol^{-1}, respectively.

RELATIVISTIC EFFECTS

Relativistic effects on the PA and EF values of H_2CO were computed by two approximate techniques. First, first-order perturbation theory was used resulting in the mass-velocity and one-electron Darwin terms (MVD1) [41, 42]. Second, the Douglas–Kroll–Hess (DKH) approach was utilized as programmed into MOLPRO. Detailed previous studies, e.g., Refs. [42 and 141], suggest that for systems such as those investigated here, the accuracy of MVD1 relative energy corrections (and thus those obtained from DKH computations) is excellent, as compared to those from more complicated multicomponent methods.

Employing the AE-CCSD(T)/aug-cc-pCVTZ level of theory and by averaging the MVD1 and DKH results, the relativistic energy shifts for the PA and EF (reaction 1) of H_2CO are −0.13 and +0.73 kJ mol^{-1}, respectively. Similar DKH results were obtained at the AE-CCSD(T)/aug-cc-pCVQZ level, suggesting that the uncertainty of the relativistic energy PA and EF (reaction 1) corrections is definitely not larger than 0.10 kJ mol^{-1}. As expected, the relativistic correction, excluding the spin-orbit effect, is largest for reaction 3, the MVD1 and DKH results obtained at the AE-CCSD(T)/aug-cc-pCVTZ level are +1.44 and +1.37 kJ mol^{-1}, respectively. The basis set dependence of these computed values is also somewhat pronounced, thus the relativistic corrections also suggest the use of reaction 1 in determining the enthalpy of formation of H_2CO.

DBOC CONTRIBUTIONS

The only feasible way to ascertain the uncertainty of the computed PA and EF values originating from the choice of determining electronic wave functions within the Born–Oppenheimer (clamped nuclei) approximation is provided by the so-called diagonal Born–Oppenheimer corrections (DBOCs) [44–47,142]. The DBOC contribution to the PA and EF (through reaction 1) values of formaldehyde, obtained at the HF/aug-cc-pVTZ level of theory, are −0.13 and +0.18 kJ mol^{-1}, respectively. DBOC contributions have also been computed for reactions 2 and 3 at the same level, they are +0.42 and −0.11 kJ mol^{-1}, respectively. These numbers confirm that it is best to use reaction 1 for the determination of the enthalpy of formation of formaldehyde and especially problematic seems to be the use of reaction 2.

DBOC corrections have also been computed at the correlated FC-CISD/aug-cc-pVDZ level. These computations provide correlation contributions to the HF DBOCs. The correlation contributions (see Table V) for the PA and EF (reaction 1) values are minuscule, −0.01 and −0.04 kJ mol^{-1}, respectively. More notable are the DBOC contributions to reactions 2 and 3. The HF DBOC for the atomization reaction is −0.11 kJ mol^{-1}, whereas the correlation contribution is a substantial +0.15 kJ mol^{-1}. This suggests some uncertainty in the BO atomization energy of H_2CO, at least at the target accuracy of this study.

In summary, it is clear that to achieve the level of accuracy sought in this study, energies from the standard Born–Oppenheimer approximation are clearly not sufficient. The uncertainty arising from the use of BO values is set to be equal to the absolute value of the DBOC corrections and the BO proton affinity and reaction enthalpy values are corrected with the computed DBOC corrections. The DBOC data support our decision that reactions 2 and 3 are not taken into account when computing the enthalpy of formation of formaldehyde.

ZERO-POINT VIBRATIONAL ENERGIES

The fully anharmonic ZPVEs of H_2CO and H_2COH^+ were obtained employing ab initio harmonic frequencies computed at the AE-CCSD(T)/aug-cc-pCVTZ level of theory and appending anharmonic corrections obtained from variational nuclear motion computations using global PESs to them. The anharmonic correction is the energy difference between the variationally computed anharmonic vibrational energy and its harmonic value corresponding to the same fitted PES. Therefore, it is likely that the uncertainty of the anharmonic correction is considerably smaller than the uncertainty of the individual harmonic and anharmonic ZPVEs. The harmonic ZPVEs (anharmonic corrections) are 69.94 (−0.73) and 106.94 (−1.58) kJ mol^{-1} for H_2CO and H_2COH^+, respectively. Our own best estimates for the anharmonic ZPVEs are thus 69.21 kJ mol^{-1} (H_2CO) and 105.36 kJ mol^{-1} (H_2COH^+). The anharmonic ZPVE determined in this study for H_2CO is consistent with an earlier accurate variational ZPVE of 69.13 kJ mol^{-1} [143], which utilized the PES of [144]. Because reproduction of the known fundamentals of formaldehyde was slightly better with the PES of [144], in what follows the ZPVE value of 69.13 kJ mol^{-1} will be used for computing the enthalpy of formation of H_2CO. Nevertheless, due to a probably favorable error compensation, our variationally corrected ZPVE estimates will be used to determine the ZPVE contribution to the PA of H_2CO, which is thus −36.15 kJ mol^{-1}. To the best of our knowledge, the present computation is the first full (9)-dimensional variational determination of the low-lying vibrational levels of the 5-atomic H_2COH^+ cation (note a recent reduced-dimensional variational vibrational study of H_2COH^+ [145]). Therefore, the ZPVE and the fundamental frequencies are reported for H_2COH^+ in Table VI. The computed anharmonic OH stretching fundamental (3,419 cm^{-1}) is in excellent agreement with the measured band of 3,423 cm^{-1} [146]. For the other vibrational modes experimental data are not available. Therefore, our computed anharmonic frequencies for H_2COH^+ provide useful guidance for future spectroscopic investigations. The ZPVE contribution to the PA of formaldehyde is believed to have an uncertainty not larger than 0.20 kJ mol^{-1}.

The variationally computed ZPVE values for H_2 and CO were taken from the literature. The ZPVE of H_2 is 26.07 kJ mol^{-1} [147]. We chose ZPVE (CO) = 12.94 kJ mol^{-1} from an experimentally derived RKR potential [148]. Thus, the ZPVE contribution to the $H_2 + CO \rightarrow H_2CO$ reaction is +30.12 kJ mol^{-1}, with an uncertainty not larger than 0.10 kJ mol^{-1}.

An extremely accurate variationally computed ZPVE is available for H_2O, it is 4638.31 cm^{-1} for $H_2{}^{16}O$ [149, 150], that is 55.49 kJ mol^{-1}, with an uncertainty not larger than 0.02 kJ mol^{-1}. This allows an accurate estimation of the ZPVE effect on reaction 2 together with the above ZPVE estimate of H_2CO.

FINAL PROTON AFFINITY AND ENTHALPY OF FORMATION AT 0 K

The final proton affinity of H_2CO at 0 K is obtained by summing the vibrationless all-electron nonrelativistic CBS FCI limit proton affinity (741.40 ± 0.30) kJ mol^{-1}, the relativistic energy shift (-0.13 ± 0.06 kJ mol^{-1}), the DBOC correction (-0.14 kJ mol^{-1}), and the ZPVE contribution (-36.15 ± 0.20 kJ mol^{-1}). Accordingly, we determine $\Delta_{pa}H_0^o(H_2CO) = 704.98 \pm 0.39$ kJ mol^{-1}. The uncertainty ascribed to this value arises mostly from electron correlation effects beyond CCSD(T) and from the uncertainty of the ZPVE of H_2COH^+. The theoretical $\Delta_{pa}H_0^o(H_2CO)$ value of Smith and Radom [34], 705.8 kJ mol^{-1}, computed using the G2 model chemistry, agrees reasonably well with our improved FPA result.

The final enthalpy of formation of H_2CO at 0 K is obtained through the reaction enthalpy of reaction 1. This is obtained by summing the vibrationless all-electron nonrelativistic CBS FCI value, -22.60 ± 0.20, the relativistic energy shift, $+0.73 \pm 0.10$, the DBOC correction, $+0.14$, and the ZPVE contribution, $+30.12 \pm 0.10$ (all in kJ mol^{-1}). Accordingly, we determine the 0 K reaction enthalpy of the $H_2 + CO \rightarrow H_2CO$ reaction as $+8.39 \pm 0.28$ kJ mol^{-1} and, consequently, $\Delta_f H_0^o(H_2CO) = -105.42 \pm 0.33$ kJ mol^{-1}. The uncertainty ascribed to this value arises mostly from higher-order electron correlation, nonadiabatic effects, and the enthalpy of formation of CO determined within the ATcT protocol. The 0 K reaction enthalpy can be compared with the value of 9.1 kJ mol^{-1} recommended by a CODATA Task Group [69].

FINAL PROTON AFFINITY AND ENTHALPY OF FORMATION AT 298.15 K

PA and EF values defined at a finite temperature, for example at 298.15 K, are of higher general utility than their 0 K counterparts and usually these are reported in databases. Therefore, the ab initio values determined in the previous subsection, referring to 0 K, need to be converted to 298.15 K. The conversion relation to a non-zero temperature (ΔH_T^o) is

$$\Delta H_T^o = \Delta H_0^o + \Delta H_{el}(T) + \Delta H_{trans}(T) + \Delta H_{vib}(T) + \Delta H_{rot}(T), \quad (3)$$

where $\Delta H_{el}(T)$, $\Delta H_{trans}(T)$, $\Delta H_{vib}(T)$, and $\Delta H_{rot}(T)$ are the temperature-dependent electronic, translational, vibrational, and rotational enthalpy contributions, respectively.

If the excited electronic states of the species involved in the thermochemical reaction are at much higher energies than the corresponding ground state, $\Delta H_{el}(T) = 0$ at 298.15 K. This holds for both reactions involving closed-shell systems considered in this present study. The $\Delta H_{trans}(T)$ contributions are $3/2RT + p\Delta V = 5/2\,RT$ (6.20 kJ mol^{-1} at 298.15 K) for PA(H_2CO), i.e. for the $H_2COH^+ \rightarrow H_2CO + H^+$ reaction, and $-3/2RT + p\Delta V = -5/2RT$ (-6.20 kJ mol^{-1} at 298.15 K) for the $H_2 + CO \rightarrow H_2CO$ reaction (reaction 1). If one assumes that the species are classical *rigid* rotors, $\Delta H_{vib}(T) = 0$ and $\Delta H_{rot}(T)$ is also zero for the PA because both H_2CO and H_2COH^+ are nonlinear, thus the classical rotational terms ($3/2RT$) cancel each other. However, for reaction 1 $\Delta H_{rot}(T) = 3/2RT - RT - RT = -1/2RT$ (-1.24 kJ mol^{-1} at 298.15 K). Therefore, the classical thermal contributions to the PA and to reaction 1 are $+6.20$ and -7.44 kJ mol^{-1} at 298.15 K, respectively. Of course, to obtain the temperature correction H^o(298.15 K) $-$ H^o(0 K) for H_2CO, the latter correction must be augmented with the similar correction for the C(graphite) + ½ $O_2 \rightarrow CO$ reaction, for which data exist in the literature, for example in Table III of [78].

Vibrational enthalpy effects can be treated by evaluating partition functions via direct summation of variationally computed vibrational energy levels. In this way, we obtained vibrational enthalpy contributions of [0.10 (H_2CO) $-$ 0.26 (H_2COH^+)] = -0.16 kJ mol^{-1} and [0.10 (H_2CO) $-$ 0.00 (H_2) $-$ 0.00 (CO)] = $+0.10$ kJ mol^{-1} to the 298.15 K PA of H_2CO and the enthalpy of the $H_2 + CO \rightarrow H_2CO$ reaction, respectively. These "quantum" corrections, which are classically zero, are certainly not negligible for our target accuracy. The difference between the vibrational effects for H_2CO and H_2COH^+ is due to the larger density of the low-lying vibrational bands of H_2COH^+ relative to the density of the vibrational states of H_2CO, i.e. there are 4 (H_2CO) and 6 (H_2COH^+) vibrational levels in the 0–1,800 cm^{-1} range above the corresponding ZPVEs. Furthermore, the low-lying fundamentals of H_2COH^+ are red-shifted with respect to the corresponding fundamentals of H_2CO. To evaluate rotational enthalpy contributions, we employed the usual rigid-rotor analytic formulas for rotational energy levels in the direct summations for the rotational partition functions. Because the (A_e, B_e, C_e) equilibrium rotational constants (in cm^{-1}) of the reference structures of H_2CO and H_2COH^+ are (9.53, 1.30, 1.14) and (6.65, 1.15, 0.98), respectively, both species are close to the symmetric top limit; thus, the analytic energy expressions of symmetric tops can be used to estimate the rotational terms of these asymmetric tops. We found that the rotational contribution to the 298.15 K PA of H_2CO is [3.71 − 3.71] = 0.00 kJ mol^{-1}, i.e. the enthalpies cancel each other and the individual results differ just slightly from the classical value (3.72 kJ mol^{-1}). In the case of the $H_2 + CO \rightarrow H_2CO$ reaction the rotational temperature effect at 298.15 K is [3.71 (H_2CO) − 2.23 (H_2) − 2.47 (CO)] = −0.99 kJ mol^{-1}. This result differs from the classical value (−1.24 kJ mol^{-1}) substantially because the rotational enthalpy of H_2 is significantly lower than the classical value (2.48 kJ mol^{-1}) as H_2 has an unusually large rotational constant (60.76 cm^{-1}).

The sum of the enthalpy effects, i.e. [$\Delta H_{\mathrm{trans}} + \Delta H_{\mathrm{vib}} + \Delta H_{\mathrm{rot}}$], yields thermal contributions of [+6.20 − 0.16 + 0.00] = +6.04 kJ mol^{-1} and [−6.20 + 0.10 − 0.99] = −7.09 kJ mol^{-1} for the 298.15 K PA of H_2CO and the enthalpy of the $H_2 + CO \rightarrow H_2CO$ reaction, respectively. The latter value must be corrected by +3.28 kJ mol^{-1}, the H^o(298.15 K) − H^o(0 K) correction for CO [78]. Therefore, we arrive at the final values of $\Delta_{\mathrm{pa}}H^{\mathrm{o}}_{298}(H_2CO) = 711.02 \pm 0.39$ kJ mol^{-1} and $\Delta_{\mathrm{f}}H^{\mathrm{o}}_{298}(H_2CO) = -109.23 \pm 0.33$ kJ mol^{-1}.

Conclusions

In a recent study [35], we anchored the proton affinity scale of organic molecules by establishing the 298.15 K PA values of CO and NH_3 as 592.4 ± 0.2 and 852.6 ± 0.3 kJ mol^{-1}, respectively. Knowledge of accurate PA values should be useful in many applications, for example in MS and MS/MS experimental studies including those related to proteomics. Certain transformation reactions important in MS, like those enhanced by proton-transport catalysis, also require an accurate knowledge of PA values of species used for the catalysis, for example that of formaldehyde [151].

In this study, the highest levels of electronic structure theory currently feasible have been employed in focal-point analyses to systematically converge on the 0 K proton affinity and enthalpy of formation of H_2CO. Another unique feature of this study is that thermal contributions to these quantities have been evaluated by direct summation of partition functions over computed rotational and variationally computed vibrational energy levels. The current report is a continuation of our methodological milestone studies for ab initio quantum chemical determination of thermochemical quantities and we pinpoint here both the PA and EF of formaldehyde to about 0.3–0.4 kJ mol^{-1}.

In the process, a number of valuable observations are made regarding the performance of state-of-the-art theoretical methods: (1) each step in the coupled-cluster series CCSD → CCSDT → CCSDTQ → CCSDTQP reduces the electron correlation error by 80% for the proton affinity and the reaction enthalpy of the reaction $H_2 + CO \rightarrow H_2CO$ involving closed-shell species, and CCSDTQ appears sufficient to converge these quantities within 0.1 kJ mol^{-1} of the full configuration interaction (FCI) limit; (2) the perturbative CCSDT(Q) method reproduces the full CCSDTQ effect quite well for both quantities; (3) conventional CCSD(T) computations with the aug-cc-pCV6Z basis have an incompleteness error of 0.34 kJ mol^{-1} of the corresponding CBS limit for the PA, though the extrapolated value agrees to 0.08 kJ mol^{-1} with the largest explicitly correlated F12 result; (4) although the extrapolated (CBS) and the F12 numbers agree very well at both the CCSD and CCSD(T) levels, it is worth mentioning that the computation combining the F12 technique with the aug-cc-pCV5Z or even with the R12-suited (19*s*14*p*8*d*6*f*4*g*3*h*)/(9*s*6*p*4*d*3*f*) basis sets are significantly less expensive than the traditional aug-cc-pCV6Z CCSD(T) computation though yielding similar accuracy; (5) one of the largest sources of uncertainty in the first-principles determination of highly accurate thermochemical quantities of polyatomic molecules is clearly the ZPVE correction; for example, use of the harmonic approximation in evaluating the effect of ZPVE on PA(H_2CO) engenders a very substantial 0.85 kJ mol^{-1} error, as the anharmonic corrections to the individual ZPVEs of H_2CO and H_2COH^+ are −0.73 and −1.58 kJ mol^{-1}, respectively; (6) the Born–Oppenheimer approximation is not satisfactory in predicting either the PA or EF (reaction 1) of H_2CO to our target accuracy, DBOCs shift these quantities by −0.14 and +0.14 kJ mol^{-1}, respectively, and in less favorable reactions (like reaction 2) the DBOC contribution can be as large as 0.4 kJ mol^{-1}; (7) the correlation contribution to the DBOC shifts, determined at the frozen-core CISD level, are comfortably small, only −0.01 and −0.04 kJ mol^{-1} for the PA and EF (reaction 1) values, respectively; (8) MVD1 and DKH relativistic effects differ insignificantly from each other and shift PA(H_2CO) and EF(H_2CO) by −0.1 and +0.7 kJ mol^{-1}, respectively; (9) neglecting terms other than the translation enthalpy of H^+ in determining the 298.15 K proton affinity of H_2CO causes a considerable error, the vibrational contribution is -0.16 kJ mol^{-1} as determined from partition functions obtained via direct summation of variationally computed vibrational energy levels; and (10) in the case of the $H_2 + CO \rightarrow H_2CO$ reaction the "quantum" rotational temperature effect at 298.15 K is -0.99 kJ mol^{-1}, differing from the classical value by as much as -0.25 kJ mol^{-1} due to the unusually large rotational constant of H_2.

The final 298.15 K results determined in this study are $\Delta_{pa}H^{o}_{298}(H_2CO) = 711.02 \pm 0.39$ kJ mol^{-1} and $\Delta_{f}H^{o}_{298}(H_2CO) = -109.23 \pm 0.33$ kJ mol^{-1}. These recommended values supersede all previous determinations due to the rigor and precision with which they have been pinpointed.

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