

Benchmarking State-of-the-Art *ab Initio* Thermochemical Predictions with Accurate Pulsed-Field Ionization Photoion–Photoelectron Measurements

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ABSTRACT

This Account presents a comparison between highly precise thermochemical data, including ionization energies, 0 K dissociative photoionization thresholds, and 0 K bond dissociation energies, of selected radicals and molecules and their cations obtained by pulsed field ionization photoion–photoelectron measurements and state-of-the-art thermochemical predictions calculated by the wavefunction-based *ab initio* CCSD(T)/CBS procedures with high-level corrections. The CCSD(T)/CBS method combines the coupled cluster approach including single, double, and quasi-perturbative triple excitations [CCSD(T)] and the complete basis set (CBS) extrapolation approximation. This benchmarking effort indicates that the CCSD(T)/CBS procedures together with high-level corrections are capable of yielding reliable thermochemical predictions with error limits ≤ 10 meV for small radicals and molecules and their cations. The error limits increase to ~ 35 meV for larger molecular species, such as phenyl and benzyl radicals.

1. Introduction

The establishment of accurate thermochemical data, such as 0 K bond dissociation energies (D_0 's) and 0 K heats of formation (ΔH_{f0}° 's), for a board range of chemical species and their ions plays a central role in the prediction of chemical reactivity and thus represents an important endeavor for the understanding of chemical transformations. On the basis of the cation cycle, thermochemical determinations may involve the measurements of ionization energies (IEs) and 0 K dissociative photoionization thresholds or appearance energies (AEs) for gaseous species. The measured IE values of a molecule AB [IE(AB)] and its fragment A [IE(A)], along with the AE for the formation of A^+ from AB [AE(A^+)], allow the

direct determination of the ionic $D_0(A^+-B)$ and neutral $D_0(A-B)$ according to eqs 1 and 2, respectively.

$$D_0(A^+-B) = AE(A^+) - IE(AB) = \Delta H_{f0}^\circ(A^+) + \Delta H_{f0}^\circ(B) - \Delta H_{f0}^\circ(AB^+) \quad (1)$$

$$D_0(A-B) = AE(A^+) - IE(A) = \Delta H_{f0}^\circ(A) + H_{f0}^\circ(B) - \Delta H_{f0}^\circ(AB) \quad (2)$$

Using appropriate thermochemical cycles, the IE and AE measurements can also be transformed into ΔH_{f0}° 's for AB/AB^+ , A/A^+ , and B/B^+ and other related species.

Equations 1 and 2 show that the precisions for $D_0(A^+-B)$ and $D_0(A-B)$ thus determined depend only on the uncertainties of $AE(A^+)$, $IE(AB)$, and $IE(A)$. Employing the high-resolution vacuum ultraviolet (VUV) laser pulsed field ionization–photoelectron (PFI–PE) method, the IEs for many small to medium-size molecules and radicals can now be determined to a precision of ≤ 0.3 meV.^{1–9} The development of the VUV synchrotron PFI–PE and PFI–PE–photoion coincidence (PFI–PEPICO) scheme has made possible the measurements of the IEs and AEs for many gaseous species with precisions of 1–3 meV.^{2,10–20} Combining these IEs and AEs has provided D_0 and ΔH_{f0}° values for many molecular species and their ions with unprecedented precisions.²

On the theoretical front, the advances in computer technology and the development of program codes have made possible the reliable prediction of thermochemical properties by *ab initio* quantum calculations. The semiempirical Gaussian-n procedures by Pople et al.²¹ and the complete basis set (CBS) extrapolation methods are among the most popular theoretical methods^{22,23} for thermochemical calculations. Meanwhile, the combination of the coupled cluster level including single, double, and quasi-perturbative triple excitations [CCSD(T)]²⁴ and the CBS extrapolation schemes [CCSD(T)/CBS] has been shown to be highly accurate for thermochemical predictions.^{22,23} Rather than using a semiempirical correction to remedy the correlation deficiency as in the Gaussian-n procedures, the CCSD(T)/CBS procedures are fully *ab initio* methods, which explicitly incorporate the zero-point vibration energy (ZPVE) correction, the core–valence electronic correlation, the scalar-relativistic correction, the spin–orbit coupling, the diagonal Born–Oppenheimer correction, and the higher order correction beyond the perturbative triple excitations. The wavefunction-based CCSD(T)/CBS scheme with these high-level corrections,²⁵ which will be referred to as CCSD(T)/CBS procedure below, was originally used by Dixon, Feller, and Peterson and is currently a state-of-the-art theoretical method for thermochemical predictions.

Considering the fact that experimental measurements can only be made on a limited number of molecular systems, a primary goal of performing experimental measurements is to provide highly precise and reliable ther-

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mochemical data for assessing the accuracy of state-of-the-art *ab initio* quantum calculations based on the first principles. With this in mind, we have made extensive comparisons between the IE, AE, D_0 , and ΔH_0° values for a broad range of molecular species and their cations obtained by PFI–PE and PFI–PEPICO measurements and by CCSD(T)/CBS calculations.^{4–9,14–19,26–29} This Account represents a review of these benchmarking efforts.

II. Experimental Methods

A. IE Measurements Using the PFI–PE Method. The most significant advance in IE measurements in the past decade has been the establishment of the PFI methods,^{1,2} which are based on the PFI of high- n Rydberg states formed in laser photoexcitation. The utilization of the PFI methods has been greatly extended by the development of tunable VUV laser and synchrotron radiation sources.² The achievable PFI–PE resolutions in VUV laser measurements are generally in the range of 0.1–3 cm^{-1} (full width at half-maximum, fwhm), as compared to those of 1–8 cm^{-1} (fwhm) for VUV synchrotron measurements.²

Although the PFI–PE resolutions are still inadequate for performing detailed rotationally resolved studies of polyatomic molecules, the VUV laser PFI–PE vibrational bands of polyatomic species often reveal rotational contours, the simulations of which have been shown to provide IEs with precisions of 1–2 cm^{-1} .^{2,4–9} The IEs^{4–9} for $\text{CHCl}=\text{CCl}_2$, *cis*-/*trans*-/*iso*- $\text{CH}_3\text{CH}=\text{CHCH}_3$, *cis*-/*trans*- $\text{C}_2\text{H}_2\text{Cl}_2$, and *cis*-/*trans*- $\text{CH}_3\text{CH}=\text{CHBr}$ determined using this approach, along with those^{2,3,11,17–19,29–31} for H_2O , D_2O , NH_3 , ND_3 , CH_4 , CD_4 , C_2H_2 , C_2H_4 , BCl_3 , CH_3Br , CH_3I , $\text{CH}_2=\text{CHBr}$, and $\text{CH}_3\text{CH}_2\text{Br}$ obtained by PFI–PE measurements, are included in Table 1.

A notable achievement in recent PFI–PE studies, particularly those performed in the Chen and Merkt laboratories,^{32–34} is the measurement of rovibrationally resolved photoelectron spectra for a series of radicals, yielding highly precise IEs for the OH, OD, CH_2 , CH_3 , C_3H_3 (propargyl), C_3H_5 (allyl), and $\text{C}_6\text{H}_5\text{CH}_2$ (benzyl) radicals.^{3,26,28,32–34} Precise IEs for C_2H , NH_2 , and ND_2 radicals have also been deduced^{10,14,17} with the AEs of C_2H^+ , NH_2^+ , and ND_2^+ from the PFI–PEPICO measurements of C_2H_2 , NH_3 , and ND_3 and known D_0 values^{35,36} for the H–CCH, H– NH_2 , and D– ND_2 bonds. The IEs for C_2H_3 , C_2H_5 , *c*- C_3H_2 (cyclopropenylidene), HCCCH (propargylene), H_2CCC (propadienylidene), 2- C_3H_7 (2-propyl), and C_6H_5 (phenyl) radicals have been determined with uncertainties of 10–40 meV by photoion–photoelectron methods.^{18,26–28,37–40} The IE values for all these radicals are also listed in Table 1.

B. AE Measurements Using the PFI–PEPICO Method.

Currently, the most general and precise procedure for AE determinations is the PFI–PEPICO method, which achieves an energy resolution of 1 meV (fwhm).^{2,10–20} Figure 1a depicts a schematic of the ground-state potential energy curves for AB and AB^+ correlating to their respective dissociation limits of $\text{A} + \text{B}$ and $\text{A}^+ + \text{B}$, while the expected breakdown curves for A^+ and AB^+ obtained using a 0 K

Table 1. Comparison of Experimental IEs [IE(exp)s] for Molecules and Radicals Measured by the PFI Methods with Theoretical IEs [IE(theo)s] Obtained by CCSD(T)/CBS Calculations^a

	IE(exp)	IE(theo)	$\Delta(\text{theo} - \text{exp})^b$
Polyatomic Molecules			
H_2O	12.6174 ± 0.0003	12.617	−0.0004
D_2O	12.6360 ± 0.0003	12.634	−0.002
NH_3	10.1864 ± 0.0001	10.185	−0.001
ND_3	10.200 ± 0.001	10.197	−0.003
CH_4	12.618 ± 0.004	12.617	−0.001
CD_4	12.6708 ± 0.0002	12.670	−0.0008
C_2H_2	11.4006 ± 0.0006	11.401	0.0004
C_2H_4	10.51268 ± 0.00003	10.514	0.0013
BCl_3	11.6410 ± 0.0002	11.606	−0.035
CH_3Br	10.5418 ± 0.0002	10.548	0.006
CH_3I	9.5382 ± 0.0002	9.523	−0.015
<i>cis</i> - $\text{CH}_3\text{CH}=\text{CHCH}_3$	9.12462 ± 0.00019	9.126	0.001
<i>trans</i> - $\text{CH}_3\text{CH}=\text{CHCH}_3$	9.12837 ± 0.00025	9.129	0.002
$\text{CH}_2=\text{C}(\text{CH}_3)_2$	9.22047 ± 0.00025	9.222	0.002
<i>cis</i> - $\text{ClCH}=\text{CHCl}$	9.65815 ± 0.00025	9.668	0.010
<i>trans</i> - $\text{ClCH}=\text{CHCl}$	9.63090 ± 0.00025	9.642	0.011
$\text{CHCl}=\text{CCl}_2$	9.4776 ± 0.0002	9.484	0.006
$\text{CH}_2=\text{CHBr}$	9.8200 ± 0.0015	9.841	−0.021
$\text{CH}_3\text{CH}_2\text{Br}$	10.307 ± 0.002	10.320	0.013
<i>cis</i> - $\text{CH}_3\text{CH}=\text{CHBr}$	9.3162 ± 0.0002	9.332	0.016
<i>trans</i> - $\text{CH}_3\text{CH}=\text{CHBr}$	9.2715 ± 0.0002	9.289	0.017
Radicals			
OH	13.017 ± 0.0003	13.014	−0.003
OD	13.0289 ± 0.0003	13.024	−0.005
NH_2	11.1633 ± 0.0025	11.160	−0.003
ND_2	11.1784 ± 0.0025	11.182	0.004
CH_2	10.3864 ± 0.0004	10.382	−0.004
CH_3	9.8380 ± 0.0004	9.839	0.001
CD_3	9.8303 ± 0.0006	9.831	0.0007
C_2H	11.645 ± 0.0014	11.650	0.005
C_2H_3	8.468 ± 0.029 ^c	8.485	0.017
C_2H_5	8.117 ± 0.008 ^c	8.119	0.002
<i>c</i> - C_3H_2	9.15 ± 0.03 ^c	9.164	0.014
HCCCH	8.96 ± 0.04 ^c	8.987	0.027
H_2CCC	10.43 ± 0.02 ^c	10.388	−0.042
C_3H_3	8.673 ± 0.001	8.679	0.006
C_3H_5	8.1535 ± 0.0006	8.158	0.004
2- C_3H_7	7.430 ± 0.027 ^c	7.436	0.006
C_6H_5	8.32 ± 0.04 ^c	8.261	−0.059
$\text{C}_6\text{H}_5\text{CH}_2$	7.2491 ± 0.0006	7.284	0.035

^a All values are in eV. ^b $\Delta(\text{theo} - \text{exp}) = \text{IE}(\text{theo}) - \text{IE}(\text{exp})$. ^c The values are not PFI values.

(dashed curves) and a 298 K (solid curves) gas sample are shown in Figure 1b. At a given VUV energy [$h\nu(\text{VUV})$] used in the PFI–PEPICO measurement, the internal excitation of AB^+ [$h\nu(\text{VUV}) - \text{IE}(\text{AB}^+)$] formed by photoionization can be controlled by varying $h\nu(\text{VUV})$. For a 0 K sample (all AB molecules are in the ground state) and at $h\nu_2 < \text{AE}(\text{A}^+)$, excited AB^+ ions are expected to form in a narrow internal energy range (determined by the PFI–PEPICO resolution) below $D_0(\text{A}^+ - \text{B})$; thus, the fractional abundance for AB^+ (A^+) is one (zero) for the 0 K sample. However, due to the Boltzmann rotational distribution of AB [shown as $P(T)$ in Figure 1a] at 298 K, some molecular ions formed from rotationally excited states of the thermal sample at $h\nu_2$ already have sufficient internal energies to dissociate, resulting in the fractional abundance for AB^+ (A^+) being less than one (greater than zero). The fact that A^+ can be formed from a thermal sample at $h\nu(\text{VUV})$ below the AE has caused a great deal of ambiguity in previous AE measurements. As $h\nu(\text{VUV})$ is increased to $h\nu_1$ [$= \text{IE}(\text{AB}) + D_0(\text{A}^+ - \text{B}) = \text{AE}(\text{A}^+)$], all excited AB^+ ions produced in the PFI–PEPICO measurement have enough internal energy to dissociate, regardless of the AB sample

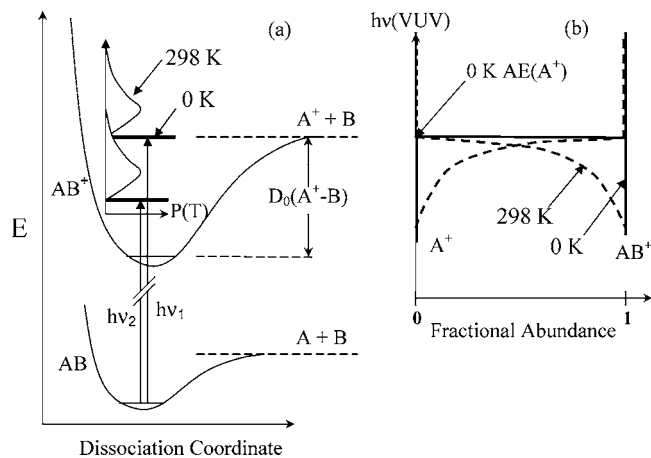


FIGURE 1. (a) Schematic diagram showing the potential energy curves of the AB and AB⁺ ground states and the energetics of the process $AB + h\nu(\text{VUV}) \rightarrow AB^{++} + e^- \rightarrow A^+ + B + e^-$, using the 0 and 298 K samples. $h\nu_1 = \text{IE}(\text{AB}) + D_0(\text{A}^+-\text{B})$ and $h\nu_2 < \text{IE}(\text{AB}) + D_0(\text{A}^+-\text{B})$. The Boltzmann rotational populations, $P(T)$, at 0 and 298 K are shown. (b) Breakdown curves for the parent AB⁺ and daughter A⁺ ions observed using a 0 K (—) and a 298 K (---) sample. For both 0 and 298 K samples, the disappearance energy for the parent AB⁺ = AE(A⁺).

temperature. If the dissociation occurs at a time scale shorter than the experimental time, the fractional abundance for AB⁺ (A⁺) should become zero (one) at $h\nu_1$. That is, the AE(A⁺) can be unambiguously determined by identifying the disappearance energy of parent AB⁺, regardless of the AB sample temperature. A great advantage of this approach is that the AE determination does not depend on any theoretical simulations of the breakdown curves.

To illustrate the AE measurement using the PFI–PE and PFI–PEPICO methods, we show in Figure 2a,b the PFI–PE spectrum of C₂H₂ and the breakdown curves for the parent C₂H₂⁺ and daughter C₂H⁺ ions observed in the PFI–PEPICO measurement of C₂H₂ at VUV energies near the AE(C₂H⁺).^{10,13} Due to the supersonic cooling of the C₂H₂ sample, the breakdown curves for C₂H₂⁺ and C₂H⁺ are sharp, showing the disappearance energy of C₂H₂⁺ [AE(C₂H⁺)] at 17.3576 ± 0.0010 eV. An interesting observation is that the PFI–PE spectrum for C₂H₂ exhibits a distinct step-like feature at the AE(C₂H⁺) as marked by the arrow in Figure 2a. This step feature has been ascribed to the “lifetime switching” effect at the AE, where excited C₂H₂ in high-*n* Rydberg states [C₂H₂^{*}(*n*)] are converted into excited C₂H fragments in high-*n*′ Rydberg states [C₂H^{*}(*n*′)] prior to PFI.^{10,13} Since these C₂H^{*}(*n*′) species are formed below the IE(C₂H) and have a longer lifetime, the PFI–PE signal derived from PFI of C₂H^{*}(*n*′) at the AE is enhanced. Similar step-like features have also been observed in the PFI–PE spectra of CD₄, C₂H₂, NH₃, H₂O, and CH₃Br at their respective AEs for the formation of CD₃⁺, C₂H⁺, NH₂⁺, OH⁺, and CH₃⁺.^{2,10,14,16} These step-like structures, together with the parent ion disappearance energies identified in PFI–PEPICO measurements, have provided unambiguous AE values for the dissociative photoionization processes.

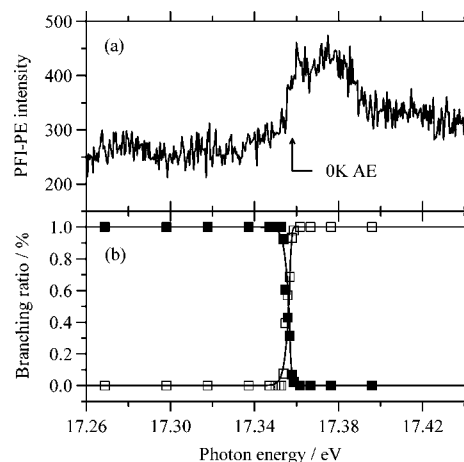


FIGURE 2. Comparison of the PFI–PE spectrum and breakdown diagram for C₂H₂: (a) PFI–PE spectrum for C₂H₂—the arrow marks the AE(C₂H⁺) from C₂H₂; (b) the breakdown curves for C₂H⁺ (□) and C₂H₂⁺ (■).

III. Theoretical Approaches

There is a wide range of *ab initio* theoretical methods available to solve the time-independent nonrelativistic electronic Schrödinger equation. Among them, wavefunction-based models such as the coupled cluster theory,⁴¹ when coupled with the convergence behavior of the one-electron basis functions, such as Dunning’s correlation consistent basis sets,⁴² are capable of approaching the exact solution in a systematic way.

A. Coupled Cluster Theory. The coupled cluster theory⁴¹ has been shown to be one of the most successful many-electron models. One of the unique characteristics of the coupled cluster theory is that it offers a systematic way of improving the single-determinant Hartree–Fock (HF) wavefunction. The fundamental equation of the coupled cluster theory is

$$\Psi_{\text{CC}} = \exp(\hat{T})\Phi \quad (3)$$

where Ψ_{CC} is the correlated molecular electronic wavefunction based on the exponential operator [$\exp(\hat{T}) = \sum_{k=0}^{\infty} \hat{T}^k/k!$] and the reference function (Φ) is the normalized HF wavefunction. The $\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \dots + \hat{T}_i$ is a cluster operator that generates excitations out of the HF determinants.

Truncation of the cluster operator at $i = 2$ and 3 leads to the CCSD and CCSDT theories, respectively. Successive inclusion of higher excitations such as quadruple (Q), pentupule (P), and so on yields the full configuration interaction solution to the electronic Schrödinger equation. However, since the coupled cluster equation has to be solved in an iterative manner, even the CCSDT model becomes very demanding for routine calculations. Thus, the treatment of the triple excitations is done by perturbation theory, leading to the CCSD(T) theory,²⁴ which is the most commonly used variant in the coupled cluster hierarchy as a compromise of efficiency and accuracy.

B. CBS Extrapolation Approximation. The hierarchy of Dunning’s correlation-consistent polarization basis

sets⁴² has been designed for recovering electron correlations in a systematic manner. When a series of these basis sets is used, the total correlation energy is found to exhibit a convergence behavior toward the limit of one-electron atomic basis functions, that is, the CBS limit. At the CBS limit, the basis set error is supposed to be zero and is isolated from the intrinsic error due to approximations of the wavefunction model. Based on the asymptotic convergence of the electronic correlation energy obtained with these basis sets, the CBS energies (E_{CBS}) have been estimated by two most commonly used three-point and two-point extrapolation schemes⁴³ as shown in eqs 4 and 5.

$$E(X) = E_{\text{CBS}} + B \exp[-(X - 1)] + C \exp[-(X - 1)^2] \quad (4)$$

$$E(X) = E_{\text{CBS}} + \frac{B}{X^3} \quad (5)$$

where $X = 2, 3, \dots, 6$ are for the (aug-)cc-pVDZ, (aug-)cc-pVTZ, ..., (aug-)cc-pV6Z basis sets,^{42,44,45} respectively. For molecules containing Cl and I atoms, the (aug-)cc-pV-($X+d$)Z basis with tight d-functions and the cc-pVXZ basis with relativistic pseudopotentials are used, respectively.⁴⁵ The CCSD(T) energy calculations are done in a frozen core fashion, that is, the 1s electrons for first-row, 1s/2s/2p electrons for second-row, and 1s/2s/2p/3s/3p/3d electrons for third-row elements are not correlated. We have used the average E_{CBS} value of the two-point and the three-point extrapolation schemes. The geometrical optimizations are performed at the CCSD(T) level with 6-311G-(2df,p) or (aug-)cc-pVTZ basis set.

C. ZPVE Calculations. In order to achieve higher accuracy for thermochemical predictions, we have included anharmonic contributions in the ZPVE calculations. We first calculated the harmonic frequencies at the CCSD(T) level, together with harmonic frequencies and anharmonic effects employing the Møller–Plesset second-order perturbation theory (MP2) or the Becke three-parameter Lee–Yang–Parr (B3LYP) exchange–correlation functionals. The CCSD(T) harmonic frequencies are then corrected with the anharmonicities obtained at the MP2 and B3LYP level to yield anharmonic frequencies effectively at the CCSD(T) level.

It has been shown⁴⁶ that the ZPVE calculation can be obtained as the average of the ZPVE from the harmonic frequencies ($\text{ZPVE}_{\text{harm}}$) and that from the anharmonic frequencies ($\text{ZPVE}_{\text{anharm}}$):

$$\text{ZPVE} = \frac{1}{2}(\text{ZPVE}_{\text{harm}} + \text{ZPVE}_{\text{anharm}}) \quad (6)$$

where $\text{ZPVE}_{\text{harm}}$ and $\text{ZPVE}_{\text{anharm}}$ are based on the CCSD(T) harmonic frequencies and effective anharmonic frequencies, respectively.

D. Corrections to the CCSD(T)/CBS Method. D.1. Core–Valence Correlation. The core–valence energy (E_{CV}) takes into account the electronic correlation contributions between the core and valence electrons and those within core electrons. The E_{CV} is calculated using the cc-

pwCVXZ basis set and is defined as

$$E_{\text{CV}} = E[\text{CCSD(T, core+valence)/cc-pwCVXZ}] - E[\text{CCSD(T, valence)/cc-pwCVXZ}] \quad (7)$$

where $E[\text{CCSD(T, valence)}]$ is the energy with only valence electrons correlated and $E[\text{CCSD(T, core+valence)}]$ is the energy with both core and valence electrons correlated. Since the basis set convergence for the CV correlation is much faster than that of the valence electronic correlation, we do not perform basis set extrapolation for the E_{CV} calculation. If the largest basis set used for a given valence electronic correlation is cc-pV5Z, the CV correlation would be calculated with the cc-pwCVQZ basis, that is, $X = Q$ in eq 7.

D.2. Other Corrections. The spin–orbit interaction energies (E_{SO} 's) for OH(² $\Pi_{3/2,1/2}$) and C, N, O, Cl, Br, and I atoms are taken as the experimental values.^{47,48} The SR energy (E_{SR}) is computed using the configuration interaction with the singles and doubles theory and is taken as the sum of the mass-velocity and one-electron Darwin terms in the Breit–Pauli Hamiltonian. For Cl- and Br-containing molecules, this simple E_{SR} correction procedure could be a source of error. The first-order mass-dependent adiabatic correction to the Born–Oppenheimer approximation (E_{DBOC}) is evaluated at the HF level. The higher-order correction (E_{HOC}) accounts for the imperfection of the CCSD(T) model by incorporating full triple and quadruple excitations and is defined as

$$E_{\text{HOC}} = E_{\text{CCSDT/basis A}} - E_{\text{CCSD(T)/basis A}} + E_{\text{CCSDTQ/basis B}} - E_{\text{CCSDT/basis B}} \quad (8)$$

The E_{HOC} could only be evaluated using the cc-pVDZ or cc-pVTZ basis sets and thus is limited to certain small molecules. More details of these correction terms can be found in refs 4–9, 18, 19, and 26–29.

IV. Comparison of Experimental and Theoretical Results

A. IE Values for Molecules and Radicals. The theoretical IEs [IE(theo)s] for the molecular species listed in Table 1 have been calculated using the theoretical CCSD(T)/CBS procedures outlined above.^{4–9,15–19,25–29} The deviation [$\Delta(\text{theo} - \text{exp})$] of the IE(theo)s with respect to the corresponding experimental IEs [IE(exp)s] are also listed in Table 1.

All IE(exp) values for the stable polyatomic molecules in Table 1 are highly precise with error limits of 0.03–4.0 meV.^{2–9,11,18,19,29–31} Excellent agreement is observed between the theoretical and experimental IE values for the small hydrides and their deuterium substitutes including H₂O, D₂O, NH₃, ND₃, CH₄, CD₄, C₂H₂, and C₂H₄, as indicated by the small IE(theo) deviations of 0.4–3.0 meV. The deviation for the IE(theo) of BCl₃ is found to be 35 meV. This relatively large deviation can be attributed to the strong perturbation of the ground-state electronic potential surface of BCl₃⁺ by two low-lying transition structures.¹⁹

The IE(theo)s for unsaturated hydrocarbons, *cis*-/*trans*-/*iso*-butenes, are also in excellent accord with their IE(exp)s with deviations of ~ 2 meV.^{4,5} The deviations of the IE(theo)s increase to 6–11 meV for the chlorine-substituted ethenes, such as *cis*-/*trans*-dichloroethene and trichloroethene, and to 16–21 meV for bromine-substituted hydrocarbons, such as vinyl bromide, ethyl bromide, and *cis*-/*trans*-bromopropene.^{6–9,11,29} In the CCSD(T)/CBS IE calculations for *cis*-/*trans*-bromopropenes, we found that the ΔE_{CBS} values obtained using the three-point and two-point extrapolations differ by 13–14 meV, indicating that the accuracy for the IE predictions for *cis*-/*trans*-bromopropene cannot be better than 14 meV.⁷ The increased errors for the IE(theo) values of larger molecules are to be expected and can be ascribed to insufficient correlation effects. This expectation is consistent with the increase in the IE(theo) deviation from 5 meV for CH₃Br to 15 meV for CH₃I.²⁹

The IE(exp) values for the radicals OH, OD, CH₂, CH₃, CD₃, C₃H₃, C₃H₅, and C₆H₅CH₂ are also highly precise with error limits of 0.3–1.0 meV.^{3,26,27,32–34} The IE(exp)s for NH₂, ND₂, and C₂H, which were deduced indirectly from AE and *D*₀ measurements, have larger error limits of 1.5–2.5 meV.^{10,13,14,17} With the exception of the IE(theo) for C₆H₅CH₂, which has a deviation of 35 meV, the IE(theo) values for all these radicals are found to deviate by ≤ 7 meV.

The IE(exp)s for C₂H₃, C₂H₅, *c*-C₃H₂, HCCCH, H₂CCC, 2-C₃H₇, and C₆H₅ have larger error limits (8–40 meV).^{18,26–28,37–40} The IE(theo) deviations for these radicals are found to be 2–60 meV.^{26–28} We note that the large IE(theo) deviations are observed for radicals with large uncertainties in their IE(exp)s. The C₂H₃⁺ and C₂H₅⁺ cations feature nonclassical H-bridged structures.²⁸ Thus, the IEs for C₂H₃ and C₂H₅, along with those for H₂CCC and C₆H₅, are difficult to measure because of the unfavorable Franck–Condon factors (FCFs) for photoionization transitions at their ionization thresholds.^{26–28} Considering that the CCSD(T)/CBS IE predictions for C₂H, C₂H₂, C₂H₄, C₃H₃, and C₃H₅ are in excellent agreement with the IE(exp) values, we expect that the IE(theo)s for similar C2–C3 hydrocarbon species, such as C₂H₃, C₂H₅, *c*-C₃H₂, HCCCH, H₂CCC, and 2-C₃H₇, have similar deviations of ≤ 7 meV. Thus, it is logical to believe that the errors of the IE(exp)s for these radicals are too large for assessing the accuracy of the CCSD(T)/CBS IE predictions. Furthermore, the comparison of experimental and theoretical results show that the IE(exp) values^{39,40} for HCCCH and C₆H₅ are likely to be too high.

The CCSD(T)/CBS IE calculation for C₆H₅CH₂ represents the most time-consuming calculation presented here. The comparison of the IE(theo) and IE(exp) for C₆H₅CH₂ can provide an idea of how the error limit of the CCSD(T)/CBS calculations “scales up” with molecular size.²⁷ As the number of electrons increases with the molecular size, the electron correlation effect becomes increasingly important. A focal-point analysis has been made to investigate the interplaying effect due to the one-particle basis set and the many-electron correlation wave-

Table 2. Comparison of AE Values for the Daughter Ions Formed from the Corresponding Parent Neutrals in Dissociative Photoionization Determined by PFI–PEPICO Measurements and CCSD(T)/CBS Calculations^a

daughter ion/ parent neutral	AE		$\Delta(\text{theo-exp})^b$
	PFI–PEPICO	CCSD(T)/CBS	
N ⁺ /N ₂	24.2884 ± 0.0010	24.276	−0.012
OH ⁺ /H ₂ O	18.116 ± 0.003	18.119	0.003
OD ⁺ /D ₂ O	18.220 ± 0.002	18.218	−0.002
NH ₂ ⁺ /NH ₃	15.765 ± 0.001	15.762	−0.003
ND ₂ ⁺ /ND ₃	15.892 ± 0.001	15.889	−0.003
CH ₃ ⁺ /CH ₄	14.323 ± 0.001	14.323	0.000
CD ₃ ⁺ /CD ₄	14.418 ± 0.001	14.420	0.002
C ₂ H ⁺ /C ₂ H ₂	17.357 ± 0.001	17.353	−0.004
CH ₃ ⁺ /CH ₃ Br	12.834 ± 0.002	12.837	0.003
CH ₃ ⁺ /CH ₃ I	12.269 ± 0.003	12.230	−0.039
CHF ₂ ⁺ /CHF ₂ Cl	12.415 ± 0.001	12.412	−0.003
CHFCl ⁺ /CHFCl ₂	11.911 ± 0.002	11.915	0.004
CHCl ₂ ⁺ /CHCl ₃	11.488 ± 0.002	11.497	0.009
CH ₂ Cl ⁺ /CH ₂ Cl ₂	12.123 ± 0.001	12.118	−0.005
CH ₂ Cl ⁺ /CH ₂ ClBr	11.509 ± 0.002	11.506	−0.003
BCl ₂ ⁺ /BCl ₃	12.495 ± 0.002	12.492	−0.003
C ₂ H ₃ ⁺ /C ₂ H ₃ Br	11.901 ± 0.002	11.890	−0.011
C ₂ H ₅ ⁺ /C ₂ H ₅ Br	11.130 ± 0.005	11.141	0.011
2-C ₃ H ₇ ⁺ /2-C ₃ H ₇ Cl	11.085 ± 0.005	11.074	−0.011
2-C ₃ H ₇ ⁺ /2-C ₃ H ₇ Br	10.455 ± 0.010	10.474	−0.019

^a All values are in eV. ^b $\Delta(\text{theo-exp}) = \text{AE}[\text{CCSD(T)/CBS}] - \text{AE}(\text{PFI-PEPICO})$.

function on the convergence behavior of the IE(theo) for C₆H₅CH₂.²⁷ The analysis reveals that the double electronic excitations make up a significant contribution of the valence electronic energy in the CCSD(T)/CBS IE(C₆H₅CH₂) prediction. Based on the trend of energetic convergence observed in the focal-point analysis, the IE(theo) deviation of 35 meV for C₆H₅CH₂ is most likely due to the unaccounted higher order post-CCSD(T) effects in the many-electron wavefunction.

B. AE Values for Dissociative Photoionization Processes. Table 2 compares the AEs for the first dissociative photoionization channels of 20 molecules determined in recent PFI–PEPICO measurements with their corresponding theoretical AEs calculated on the basis of the CCSD(T)/CBS procedures.^{2,10–20,29} With exception to the PFI–PEPICO AEs^{11,12} of C₂H₅Br, 2-C₃H₇Cl, and 2-C₃H₇Br, which have error limits of 5–10 meV, the PFI–PEPICO AEs of all the remaining molecules have precisions of 1–3 meV. We note that an AE(2-C₃H₇⁺) = 11.036 ± 0.010 eV was reported in a recent velocity imaging threshold electron–photoion coincidence study of 2-C₃H₇Br.⁴⁹ For H₂O, D₂O, NH₃, ND₃, CH₄, CD₄, and C₂H₂, the deviations [$\Delta(\text{theo-exp})$ s] of the CCSD(T)/CBS AEs with respect to the PFI–PEPICO AEs are well within ± 4 meV. For the Cl- and Br-containing molecular systems, the deviations for the CCSD(T)/CBS AE predictions are higher but still within 19 meV. The largest deviation (39 meV) is observed for the CCSD(T)/CBS prediction of AE(CH₃⁺) from CH₃I.²⁹

The PFI–PEPICO AE(N⁺) from N₂ has allowed the determination of the $\Delta H_{\text{f}}^{\circ}(\text{N})$ (112.46 ± 0.012 kcal/mol) with an error limit about 6-fold smaller than that of the previously accepted $\Delta H_{\text{f}}^{\circ}(\text{N})$ value.²⁰ Since the *ab initio* calculation of $\Delta H_{\text{f}}^{\circ}$ values of N-containing compounds using the atomization scheme requires calibration with the experimental $\Delta H_{\text{f}}^{\circ}(\text{N})$, this improved precision for the experimental $\Delta H_{\text{f}}^{\circ}(\text{N})$ will also improve the ac-

Table 3. Comparison of Experimental and CCSD(T)/CBS D_0 Values for Neutrals and Ions^a

neutral/ionic bonds	$D_0(\text{exp})$ neutral/ion	$D_0(\text{theo})$ neutral/ion	$\Delta(\text{theo-exp})^b$ neutral/ion
H–OH/H–OH ⁺	5.100 ± 0.003/5.499 ± 0.003	5.105/5.502	0.005/0.003
D–OD/D–OD ⁺	5.196 ± 0.003/5.584 ± 0.002	5.194/5.584	–0.002/0.000
H–NH ₂ /H–NH ₂ ⁺	4.6017 ± 0.0025/5.5786 ± 0.0010	4.602/5.577	0.000/–0.002
D–ND ₂ /D–ND ₂ ⁺	4.7126 ± 0.0025/5.691 ± 0.001	4.707/5.692	–0.0056/0.001
H–CH ₃ /H–CH ₃ ⁺	4.485 ± 0.001/1.705 ± 0.004	4.484/1.706	–0.001/0.001
D–CD ₃ /D–CD ₃ ⁺	4.588 ± 0.001/1.748 ± 0.001	4.589/1.749	0.001/0.001
H–C ₂ H/H–C ₂ H ⁺	5.7125 ± 0.0010/5.957 ± 0.001	5.703/5.952	–0.010/–0.005
Br–CH ₃ /Br–CH ₃ ⁺	2.996 ± 0.002/2.291 ± 0.002	2.998/2.289	0.002/–0.002
I–CH ₃ /I–CH ₃ ⁺	2.431 ± 0.003/2.731 ± 0.003	2.391/2.707	–0.040/–0.024
Cl–BCl ₂ ⁺ ^c	0.854 ± 0.002	0.886	0.032
Br–C ₂ H ₃ /Br–C ₂ H ₃ ⁺	3.433 ± 0.030/2.081 ± 0.003	3.405/2.049	–0.026/–0.032
Br–C ₂ H ₅ /Br–C ₂ H ₅ ⁺	3.013 ± 0.009/0.823 ± 0.005	3.022/0.821	0.009/–0.002

^a All values are in eV. ^b $\Delta(\text{theo-exp}) = D_0(\text{theo}) - D_0(\text{exp})$. ^c No data available for the neutral species.

curacy for *ab initio* ΔH_{00}° calculations of N-containing compounds. The CCSD(T)/CBS AE(N⁺) from N₂ has a relatively large deviation of 12 meV with respect to the experimental value, which can be ascribed to insufficient accounting of the higher-order correlation effect.⁵⁰

C. D_0 Values for Molecules and Their Ions. Using the IE and 0 K AE values obtained from the PFI–PE and PFI–PEPICO measurements, we have determined the D_0 values^{2,10,11,13–19} for the H–OH, H–OH⁺, D–OD, D–OD⁺, N–NH₂⁺, D–ND₂⁺, H–CH₃, H–CH₃⁺, D–CD₃, D–CD₃⁺, H–C₂H, H–C₂H⁺, Cl–BCl₂⁺, Br–CH₃, Br–CH₃⁺, I–CH₃, I–CH₃⁺, Br–C₂H₃, Br–C₂H₃⁺, Br–C₂H₅, and Br–C₂H₅⁺ bonds as shown in Table 3. The D_0 's for H–NH₂, D–ND₂, and H–C₂H measured using the H(D)-Rydberg tagging TOF technique^{35,36} are also included in Table 3. A significant result of the PFI–PE and PFI–PEPICO measurements and state-of-the-art *ab initio* calculations¹⁶ is that the previous literature values for $D_0(\text{H–OH})$ and $\Delta H_{00}^{\circ}(\text{OH})$ are found to be too high by 0.45 kcal/mol.

As shown in Table 3, the CCSD(T)/CBS D_0 values for all the neutral and ionic bonds are in excellent agreement with the corresponding experimental D_0 values with absolute deviations of ≤ 12 meV, except those for the Cl–BCl₂⁺, I–CH₃/I–CH₃⁺, and Br–C₂H₃/Br–C₂H₃⁺ bonds, where the deviations are found to be in the range of 24–40 meV.

V. Summaries

The recent developments of the high-resolution PFI–PE method for IE measurements and PFI–PEPICO scheme for AE measurements have allowed the determination of the D_0 values for small neutral and ionic species with unprecedented precisions. The IE, AE, and D_0 values for a series of small molecules and their ions determined using the PFI methods have been used for benchmarking state-of-the-art wavefunction-based CCSD(T)/CBS calculations. The comparison between the experimental and theoretical results supports the conclusion that highly accurate IE, AE, and D_0 predictions with error limits of ≤ 10 meV for small molecules and radicals can be obtained using the CCSD(T)/CBS procedures. As expected, the errors for the CCSD(T)/CBS predictions will increase as the molecular species under study becomes larger. For C₆H₅CH₂ and Cl- and Br-containing C2–C3 hydrocarbons,

the CCSD(T)/CBS predictions are generally found to have errors of < 40 meV.

The detailed comparisons between accurate experimental measurements and theoretical predictions reveal that the extrapolation schemes and various methods for ZPVE corrections contribute to a significant portion of error in the CCSD(T)/CBS calculations. It is found that both extrapolation schemes yield very similar extrapolated CBS limits for small molecules, whereas the difference in the extrapolated CBS limits between the two schemes could be as large as 14 meV for bigger molecular systems. Although the present ZPVE evaluation based on the CCSD(T) harmonic vibrational frequencies with the MP2 and B3LYP anharmonicity corrections is superior to the general ZPVE estimation based on scaled harmonic frequencies, we found that the E_{ZPVE} correction based on the MP2 anharmonicity correction can still be different from that based on the B3LYP anharmonicity correction. Since we do not know which extrapolation scheme or which anharmonicity correction method is superior, it is perhaps justifiable to use the average of the CBS limits of two extrapolation schemes and the average of the E_{ZPVE} corrections based on the MP2 and B3LYP anharmonicity corrections in the CCSD(T)/CBS calculations.

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