

LETTERS

Evidence for a Lower Enthalpy of Formation of Hydroxyl Radical and a Lower Gas-Phase Bond Dissociation Energy of Water

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There are two experimental approaches to determining $\Delta H_{f0}^{\circ}(\text{OH})$, which produce values of this key thermodynamic quantity that differ by >0.5 kcal/mol. The apparent uncertainty of the positive ion cycle approach resides in the measurement of the appearance energy of OH^+ from H_2O , while the uncertainty of the spectroscopic approach resides in the determination of the dissociation energy of $\text{OH}(\text{A}^2\Sigma^+)$. In this note we present an independent experimental determination of the appearance energy that confirms the accuracy and enhances the precision of the existing positive ion cycle value for $\Delta H_{f0}^{\circ}(\text{OH})$. We also present electronic structure calculations of the $\text{OH}(\text{A}^2\Sigma^+)$ potential energy curve, which suggest that the extrapolation method used to obtain the spectroscopic dissociation energy is in error. Finally, we present the largest ab initio electronic structure calculations ever performed for $\Delta H_{f0}^{\circ}(\text{OH})$ that have an apparent uncertainty much less than 0.5 kcal/mol and support only the positive ion cycle value. Although all major thermochemical tables recommend a value of $\Delta H_{f0}^{\circ}(\text{OH})$ based on the spectroscopic approach, the correct value is that of the positive ion cycle, $\Delta H_{f0}^{\circ}(\text{OH}) = 8.83 \pm 0.09$ kcal/mol, $D_0(\text{H}-\text{OH}) = 117.57 \pm 0.09$ kcal/mol, and $D_0(\text{OH}) = 101.79 \pm 0.09$ kcal/mol.

Introduction

The O–H bond dissociation energy of water, $D_0(\text{H}-\text{OH})$, is of fundamental importance because of the ubiquity of the OH radical in environmental, industrial, and combustion processes. Its correct value, together with the corresponding enthalpy of formation of hydroxyl radical, $\Delta H_{f0}^{\circ}(\text{OH})$, are crucial constituents of any serious thermochemical table because the properties of many other species are measured with reference to this bond energy. Realistic models to describe the chemical behavior of

complex systems, such as those common in atmospheric or combustion processes, contain hundreds of reactions, many of which are sensitive to minute inaccuracies in the enthalpies of formation of a key highly reactive species such as OH.

The comprehensive thermochemical table by Gurvich et al.¹ gives the formation enthalpy of OH as $\Delta H_{f0}^{\circ}(\text{OH}) = 9.35 \pm 0.05$ kcal/mol, from which the best available² $D_0(\text{H}-\text{OH})$ becomes 118.08 ± 0.05 kcal/mol [assuming the accepted^{1,3–5} values for $\Delta H_{f0}^{\circ}(\text{H}_2\text{O})$ and $\Delta H_{f0}^{\circ}(\text{H})$]. Gurvich et al.¹ use $D_0(\text{OH}, \text{X}^2\Pi_{3/2}) = 35420 \pm 15$ cm^{−1} (101.27 ± 0.04 kcal/mol) of Carlone and Dalby⁶ (see Table 1), which is based on a short extrapolation (~ 1.5 vibrational levels) of $\Delta G_{v+1/2}$ of the $\text{A}^2\Sigma^+$ state, yielding $D_0(\text{OH}, \text{A}^2\Sigma^+) = 18847 \pm 15$ cm^{−1} to O ¹D₂.

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TABLE 1: Various Values for the 0 K Enthalpy of Formation of OH and Related Values for $D_0(\text{H}-\text{OH})$ and $D_0(\text{OH})^a$

source	$\Delta H_{\text{f}0}^\circ(\text{OH})$	$D_0(\text{H}-\text{OH})$	$D_0(\text{OH})$
Gurvich et al., ^b following Carlone and Dalby ^c	9.35 ± 0.05 kcal/mol	118.08 ± 0.05 kcal/mol ^d (41301 ± 17 cm ⁻¹)	101.27 ± 0.04 kcal/mol (35420 ± 15 cm ⁻¹)
Barrow ^e	9.26 ± 0.29 kcal/mol	118.00 ± 0.29 kcal/mol ^d (41270 ± 100 cm ⁻¹)	101.36 ± 0.29 kcal/mol (35450 ± 100 cm ⁻¹)
JANAF ^f	9.18 ± 0.29 kcal/mol	117.91 ± 0.29 kcal/mol ^d (41240 ± 100 cm ⁻¹)	101.44 ± 0.29 kcal/mol (35480 ± 100 cm ⁻¹)
recommended values, present experiment ^g	8.83 ± 0.09 kcal/mol	117.57 ± 0.09 kcal/mol (41120 ± 30 cm ⁻¹)	101.79 ± 0.09 kcal/mol ^h (35600 ± 30 cm ⁻¹)
present calculation	8.87 ± 0.16 kcal/mol	117.61 ± 0.16 kcal/mol ^d (41135 ± 55 cm ⁻¹)	101.74 ± 0.16 kcal/mol (35585 ± 55 cm ⁻¹)

^a The total atomization energy of water at 0 K is taken to be $\Delta H_{\text{atomization}0}(\text{H}_2\text{O}) = 219.355 \pm 0.024$ kcal/mol (76721 ± 8 cm⁻¹), from refs 1, 3 and 4; see also ref 5. ^b Reference 1. ^c Reference 6, spectroscopic determination of $D_0(\text{OH})$. ^d From $\Delta H_{\text{atomization}0}(\text{H}_2\text{O}) - D_0(\text{OH})$. ^e Reference 9, spectroscopic determination of $D_0(\text{OH})$. ^f References 4 and 7, see also ref 8. ^g On the basis of the present result $\text{AE}_0(\text{OH}^+/\text{H}_2\text{O}) = 18.115 \pm 0.004$ eV (in virtually perfect agreement with the slightly coarser value of 18.115 ± 0.008 eV from ref 12) and $\text{IE}(\text{OH}) = 104989 \pm 2$ cm⁻¹ from ref 13.

^h From $\Delta H_{\text{atomization}0}(\text{H}_2\text{O}) - D_0(\text{H}-\text{OH})$.

To further substantiate their value, Carlone and Dalby measured $D_0(\text{OD}, \text{A}^2\Sigma^+)$, producing a congruent $D_0(\text{OD})$, and forwarded as additional corroborative evidence the patterns of broadening of rotational lines in OH and OD, attributed to predissociation. Other more widely used thermochemical tables, such as JANAF⁴ or the NIST-JANAF Tables⁷ list $\Delta H_{\text{f}0}^\circ(\text{OH}) = 9.18 \pm 0.29$ kcal/mol⁸ (see Table 1) because they reference an earlier measurement of $D_0(\text{OH}, \text{A}^2\Sigma^+)$ by Barrow⁹ that involves a longer and therefore more uncertain extrapolation than the subsequent and more accurate measurements of Carlone and Dalby.⁶ Inexplicably, JANAF⁴ and NIST-JANAF⁷ lower without reference⁸ the $\Delta H_{\text{f}0}^\circ(\text{OH}) = 9.26 \pm 0.29$ kcal/mol value implied by Barrow by 0.08 kcal/mol to arrive at the value quoted above.

In contrast to the recommended² $D_0(\text{H}-\text{OH})$ implied by Gurvich et al.,¹ the positive ion thermochemical cycle appears to suggest a significantly lower value, as noted by Berkowitz et al.^{2,10} This is surprising, since the positive ion cycle has a track record of yielding accurate and reliable experimental bond energies from photoionization and photoelectron measurements. In this case the cycle involves the 0 K appearance energy of the OH^+ fragment from water, $\text{AE}_0(\text{OH}^+/\text{H}_2\text{O})$, and the adiabatic ionization energy of OH, $\text{IE}(\text{OH})$, from which $D_0(\text{H}-\text{OH}) = \text{AE}_0(\text{OH}^+/\text{H}_2\text{O}) - \text{IE}(\text{OH})$. $\text{AE}_0(\text{OH}^+/\text{H}_2\text{O})$ was initially reported¹¹ (without any correction for the internal energy) as a “sharp onset” at 18.05 eV. McCulloh¹² subsequently performed a very detailed photoionization study, providing a value $\text{AE}_0(\text{OH}^+/\text{H}_2\text{O}) = 18.115 \pm 0.008$ eV, which has not been challenged since. $\text{IE}(\text{OH}) = 104989 \pm 2$ cm⁻¹ $\equiv 13.01698 \pm 0.00025$ eV is known from a ZEKE study,¹³ which was preceded^{14–16} and followed¹⁷ by other photoelectron studies giving 13.01 eV. Earlier photoionization values,^{11,12,18} which are lower, are really indirect, hinging, inter alia, on auxiliary thermochemical values, including $\Delta H_{\text{f}0}^\circ(\text{OH})$. Recent photoionization studies of the OH radical^{19–21} also suggest lower onsets, but that effect is attributed to rotational hot bands.^{20,21} Taking the best available values,^{12,13} $\text{AE}_0(\text{OH}^+/\text{H}_2\text{O}) = 18.115 \pm 0.008$ eV and $\text{IE}(\text{OH}) = 13.0170 \pm 0.0003$ eV, results in $D_0(\text{H}-\text{OH}) = 117.56 \pm 0.18$ kcal/mol, implying $\Delta H_{\text{f}0}^\circ(\text{OH}) = 8.83 \pm 0.18$ kcal/mol and $D_0(\text{OH}) = 35600 \pm 65$ cm⁻¹ (101.79 ± 0.18 kcal/mol). This value of $\Delta H_{\text{f}0}^\circ(\text{OH})$ is more than 0.5 kcal/mol lower than that of Gurvich et al.,¹ and the difference is more than twice the sum of the error bars assigned to the two values.

Such a large difference between the two values implies that at least one of the following has to be true: (a) the spectroscopic $D_0(\text{OH}, \text{A}^2\Sigma^+)$ is too low; (b) $\text{IE}(\text{OH})$ is too high; (c) $\text{AE}_0(\text{OH}^+/\text{H}_2\text{O})$ is too low.

Hypothesis b appears to be the least probable of the three, since close examination suggests that all relevant peaks of OH/OD are clearly visible in the photoelectron spectra, although strong impurity signals congest the region of interest.^{14–17} Furthermore, rotationally resolved structure in the ZEKE spectrum¹³ serves as an effective fingerprint to distinguish OH from impurities, and the experimental difference $\text{IE}(\text{OD}) - \text{IE}(\text{OH}) = 96 \pm 3$ cm⁻¹ is very close to the expected value.²²

To distinguish between spectroscopic- and photoionization-based values of $\Delta H_{\text{f}0}^\circ(\text{OH})$, we have done three studies: (1) examined hypothesis c by experimentally remeasuring $\text{AE}_0(\text{OH}^+/\text{H}_2\text{O})$ to eliminate problems such as a wavelength calibration error or an inaccurate extrapolation of the onset, (2) examined hypothesis a by carrying out ab initio electronic structure calculations on $\text{OH}(\text{A}^2\Sigma^+)$ to test the reliability of the extrapolation method used by Carlone and Dalby to obtain $D_0(\text{OH}, \text{A}^2\Sigma^+)$, and (3) theoretically directly determined $\Delta H_{\text{f}0}^\circ(\text{OH})$ to an uncertainty much less than 0.5 kcal/mol by carrying out the highest level ab initio electronic structure calculations ever performed on this system.

Studies of Hypothesis c

The basic photoionization apparatus used to remeasure $\text{AE}_0(\text{OH}^+/\text{H}_2\text{O})$ has been recently described elsewhere.²³ Small Ne I emission lines superimposed on the He Hopfield continuum provided an accurate internal energy calibration. The light intensity was monitored by an external photomultiplier, coupled to a sodium salicylate transducer. $\text{AE}_0(\text{OH}^+/\text{H}_2\text{O})$ was extracted from fragment photoion yield curves by fitting with a model function employing a procedure described in detail elsewhere.²⁴ The fit produces $\text{AE}_0(\text{OH}^+/\text{H}_2\text{O}) = 18.115 \pm 0.004$ eV, in perfect agreement with the value of McCulloh.¹² While the level of agreement is admittedly fortuitous, given the error bars, for hypothesis c to hold, the threshold in question would need to have other, more mysterious problems. However, presently it is not clear what those problems might be.

Studies of Hypothesis a

The Birge–Sponer extrapolation used by Carlone and Dalby⁶ to obtain $D_0(\text{OH}, \text{A}^2\Sigma^+)$ is notorious for inaccuracies, particularly when excited electronic states are used.^{25,26} However, the Carlone and Dalby extrapolation is extremely short and reproduces the expected isotope effect. To test this extrapolation, multireference single and double excitation (CAS+1+2 with Davidson correction) calculations²⁷ were carried out on the $\text{OH}(\text{A}^2\Sigma^+)$ potential curve with an aug-cc-pV5Z basis set.²⁸

The computed dissociation energy is not expected to be accurate to more than ~ 0.5 kcal/mol, but the number of bound levels in both OH and OD is exactly the same (10 and 14, respectively) as that deduced by Carlone and Dalby.⁶ Applying the same Birge–Sponer extrapolation to the theoretical levels that are analogous to those directly measured by Carlone and Dalby produced an estimate of $D_0(\text{OH}, \text{A}^2\Sigma^+)$ for the theoretical curve that was 115 cm^{-1} below that of the corresponding computed dissociation limit. This suggests that hypothesis a might well be correct.

Direct Ab Initio Calculation of $\Delta H_{f0}^\circ(\text{OH})$

To provide a completely independent determination of $\Delta H_{f0}^\circ(\text{OH})$, CCSD(T)/aug-cc-pVnZ, ab initio electronic structure calculations^{28,29} were carried out for OH, OH⁺, and H₂O. These calculations are by far the highest-level ab initio electronic structure calculations ever done for this system. The calculations were performed using MOLPRO, Gaussian 98, and ACESII.³⁰ The geometries were optimized at the frozen core CCSD(T) level of theory. Frozen core energies were extrapolated to the complete basis set limit energies by using a mixed exponential/Gaussian expression³¹ from aug-cc-pVnZ ($n = \text{T, Q, 5, 6}$) sequences calculated at the RCCSD(T)³² level for closed shell and R/UCCSD(T)³³ level for open shell species.³⁴ Core/valence corrections were obtained from fully correlated CCSD(T) calculations with the cc-pCV5Z basis sets at the CCSD(T)/aug-cc-pVTZ geometries. Molecular scalar relativistic corrections were included using the uncontracted cc-pVQZ basis set and the frozen core RCCSD(T) level of theory. Zero point energies were taken from experiments and include anharmonic corrections.^{22,35} Corrections for higher order excitations were based on full configuration interaction (FCI) using cc-pVTZ for OH and OH⁺, and cc-pVTZ on oxygen and cc-pVDZ on hydrogens for H₂O.

The final atomization energies, which include corrections for spin–orbit interaction in the ³P state of O and ²Π state of OH,^{22,36} are $D_0(\text{OH}) = 101.59$ kcal/mol and $\Delta H_{\text{at}0}^\circ(\text{H}_2\text{O}) = 219.04$ kcal/mol. It should be noted that the calculated atomization energies are likely to be lower limits to the correct results. The experimental atomization energy of water^{1,3–5} (219.35 ± 0.024 kcal/mol) can serve as a benchmark to estimate the amount of error; the computed result is too low by 0.31 kcal/mol. The computed IE(OH) = 300.03 kcal/mol = 13.011 eV is also expected to be a lower limit, but the error should be slightly less. Indeed, the experimental IE(OH) is larger by 6.3 meV or 0.15 kcal/mol. Hence, $D_0(\text{OH}) \geq 101.59$ kcal/mol, but probably not larger than 101.90 kcal/mol, or $35530\text{ cm}^{-1} \leq D_0(\text{OH}) \leq 35640\text{ cm}^{-1}$. Clearly, this indicates that the determination of Carlone and Dalby⁶ is too low by at least 110 cm^{-1} , and probably by $\sim 170 \pm 60\text{ cm}^{-1}$. The range of dissociation energies of OH given above translates into $9.03\text{ kcal/mol} \geq \Delta H_{f0}^\circ(\text{OH}) \geq 8.72\text{ kcal/mol}$, which is equivalent to $8.87 \pm 0.16\text{ kcal/mol}$ (see Table 1). The selection of Gurvich et al.¹ is clearly outside this range. Even the unexplained selection by JANAF^{4,7} is above this range, but the error bars allow for a slight overlap with the upper limit of the computed value. In contrast to this, the result suggested by the positive ion cycle, $\Delta H_{f0}^\circ(\text{OH}) = 8.83 \pm 0.09\text{ kcal/mol}$, or $D_0(\text{OH}) = 35600 \pm 30\text{ cm}^{-1}$, appears to be very comfortably in the middle of the computed range.

Conclusion

All major thermochemical tables recommend values for $\Delta H_{f0}^\circ(\text{OH})$ derived from the spectroscopic approach, whose

most comprehensive application leads to $D_0(\text{OH}) = 35420 \pm 15\text{ cm}^{-1}$ and hence $\Delta H_{f0}^\circ(\text{OH}) = 9.35 \pm 0.05\text{ kcal/mol}$. Contrary to this, the positive ion cycle approach, which is based on photoionization and photoelectron measurements, leads to $\Delta H_{f0}^\circ(\text{OH})$ that is lower by $\sim 0.5\text{ kcal/mol}$. In this study we have remeasured the key value entering the positive ion cycle, namely the appearance energy of OH⁺ from H₂O, and obtained $18.115 \pm 0.004\text{ eV}$, in complete accord with the slightly less precise literature value. Together with the existing value for the ionization energy of OH, the new measurement produces $\Delta H_{f0}^\circ(\text{OH}) = 8.83 \pm 0.09\text{ kcal/mol}$. We have used high quality electronic structure calculations to critique the method used experimentally to extract from the measured data the key property in the spectroscopic approach, namely the dissociation energy of OH(A²Σ⁺). This critique indicates that the extrapolation is in error in a direction that supports the positive ion cycle value for $\Delta H_{f0}^\circ(\text{OH})$. Finally, we present the highest level ab initio electronic calculations ever performed on this system to directly calculate $\Delta H_{f0}^\circ(\text{OH})$ to an error much less than the difference between the two contending values. Only the positive ion cycle value falls within the error bar of the computed value, $\Delta H_{f0}^\circ(\text{OH}) = 8.87 \pm 0.16\text{ kcal/mol}$. Thus, we believe that the best available experimental value is $\Delta H_{f0}^\circ(\text{OH}) = 8.83 \pm 0.09\text{ kcal/mol}$, based on $D_0(\text{H–OH}) = 41120 \pm 30\text{ cm}^{-1}$ ($117.57 \pm 0.09\text{ kcal/mol}$) and implying $D_0(\text{OH}) = 35600 \pm 30\text{ cm}^{-1}$ ($101.79 \pm 0.09\text{ kcal/mol}$). The corresponding 298 K values are $\Delta H_{f298}^\circ(\text{OH}) = 8.89 \pm 0.09\text{ kcal/mol}$, $D_{298}(\text{H–OH}) = 118.79 \pm 0.09\text{ kcal/mol}$, and $D_{298}(\text{OH}) = 102.77 \pm 0.09\text{ kcal/mol}$. A forthcoming paper will provide a more detailed account of the experimental and computational results mentioned here and their implications.

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- (7) Chase, M. W., Jr. *NIST-JANAF Thermochemical Tables*, 4th ed.; *J. Phys. Chem. Ref. Data* **1998**, Monograph No. 9.
- (8) A different value, $\Delta H_{f0}^\circ(\text{OH}) = 9.26 \pm 0.29\text{ kcal/mol}$, which correctly results from the selected $D_0(\text{OH}) = 35450 \pm 100\text{ cm}^{-1}$ (following Barrow⁹) is quoted explicitly in the discussion of

JANAF^{4,7} together with the remark that it "is in good agreement with the last JANAF selection", namely $\Delta H_f^\circ(\text{OH}) = 9.29 \pm 0.3$ kcal/mol from: Stull, D. R.; Prophet, H. *JANAF Thermochemical Tables*, 2nd ed.; NSRDS-NBS 37; U.S. Government Printing Office: Washington, DC, 1971. The latter value is also based on Barrow,⁹ but for some reason the adopted $D_0(\text{OH})$ was 35440 ± 100 cm⁻¹. However, the actual table of thermochemical properties^{4,7} inexplicably lists and uses $\Delta H_f^\circ(\text{OH}) = 9.175 \pm 0.29$ kcal/mol [which corresponds to $D_0(\text{OH}) = 35480 \pm 100$ cm⁻¹].

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