

## On the Determination of Monomer Dissociation Energies of Small Water Clusters from Photoionization Experiments

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Received: November 5, 2007; In Final Form: December 17, 2007

Recently, monomer dissociation energies of neutral water clusters were estimated via a thermodynamic cycle that utilized the measured appearance energies of vacuum ultraviolet (VUV) photoionized water clusters and the previously reported dissociation energies of protonated water clusters. The thermodynamic cycle incorrectly assumed that the energy difference between the  $(\text{H}_2\text{O})_n^+ \rightarrow (\text{H}_2\text{O})_{n-1}\text{H}^+ + \text{OH}^\bullet$  asymptotes (the relaxation energy) was zero. We show that these relaxation energies are large and cannot be neglected in the analysis. Thus, the neutral water cluster monomer dissociation energies *cannot* be directly determined from the measured ionization potentials because they are themselves involved in the appropriate thermodynamic cycle.

Small water cluster dissociation energies are important in many physical and chemical processes such as atmospheric aerosol formation, biological processes, steam re-forming, etc. In addition, accurate estimates of the neutral water cluster binding energies represent a key component in the development and parametrization of force fields<sup>1</sup> as well as density functional methods such as the X3LYP functional<sup>2</sup> that are used to simulate hydration phenomena in important chemical and biological processes. Understanding the evolution of water monomer dissociation energies from water clusters as a function of cluster size has received much attention. For the water dimer, an association enthalpy  $\Delta H = -3.59 \pm 0.5$  kcal/mol has been obtained<sup>3</sup> from measurements of the thermal conductivity of  $\text{H}_2\text{O}$  vapor in the temperature range  $T = 358\text{--}386$  K corresponding to a dimer binding energy  $D_e = -5.44 \pm 0.7$  kcal/mol. These values are consistent with the results of high-level electronic structure calculations.<sup>4</sup> For the larger clusters, however, energetic information has been, up to now, exclusively obtained from high-level ab initio electronic structure calculations.<sup>5</sup>

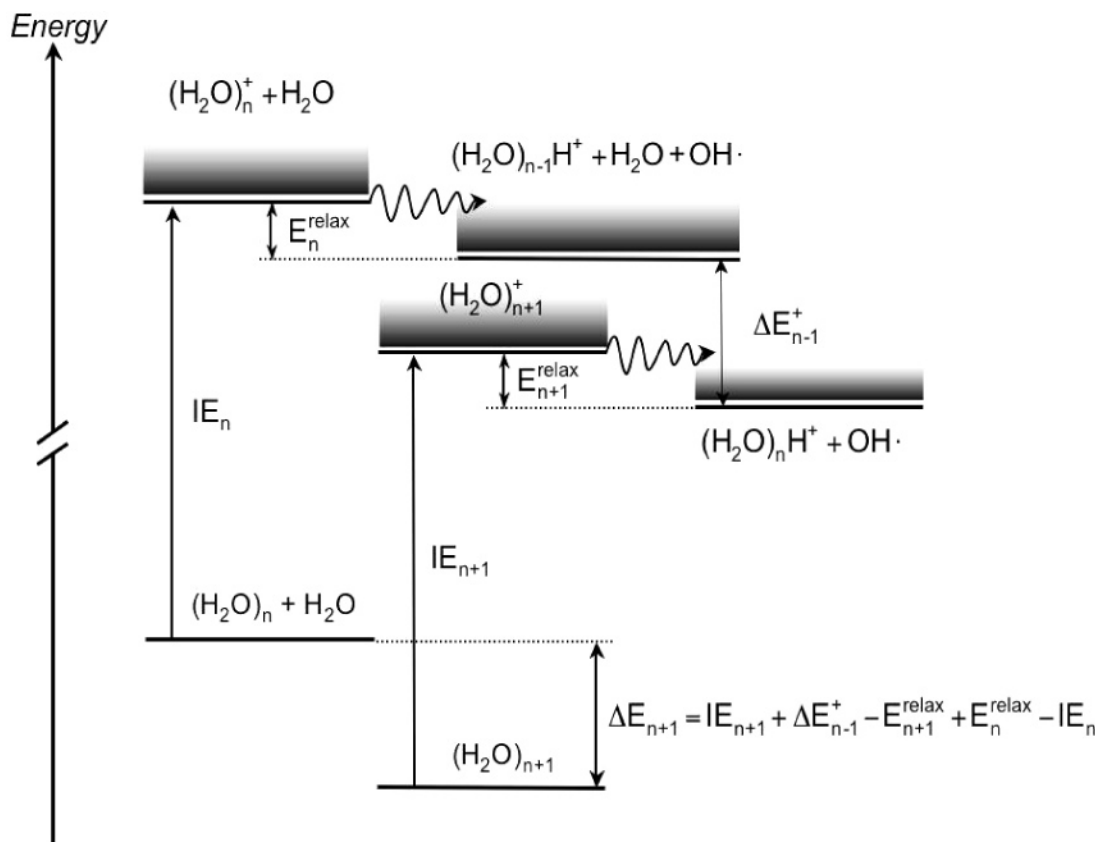
Recently, Belau et al.<sup>6</sup> have measured the vacuum ultraviolet (VUV) photoionization of small water clusters and have used those measurements to estimate (via a thermodynamic cycle shown in Figure 1) water monomer dissociation energies of neutral water clusters. In the experimental analysis of Belau et al., the “relaxation energy”,  $E_n^{\text{relax}}$ , of the VUV photoionized water cluster  $(\text{H}_2\text{O})_n^+$ , i.e., the difference between the energy levels for the process  $(\text{H}_2\text{O})_n^+ \rightarrow (\text{H}_2\text{O})_{n-1}\text{H}^+ + \text{OH}^\bullet$ , was assumed to be zero ( $E_n^{\text{relax}} = 0$ ,  $n \geq 1$ ). *In general, these energy levels are not degenerate.* The zero relaxation assumption is unjustified. Our theoretical analysis provides an accurate estimate of the relaxation energy that must be included in the interpretation of the experimental results. In the analysis of Belau et al., where the zero relaxation assumption was made, the

measured ionization (appearance) energies,  $\text{IE}_n$ , were related to the water monomer dissociation energies,  $\Delta E_{n+1}$ , from a  $(n+1)$ -mer water cluster via

$$\Delta E_{n+1} = (\text{IE}_{n+1} - \text{IE}_n) + \Delta E_{n-1}^+ \quad (1)$$

where  $\Delta E_{n-1}^+$  is the dissociation energy of a water monomer from a  $n$ -mer protonated water cluster  $(\text{H}_2\text{O})_n\text{H}^+$ . This analysis also assumed the availability of reliable relative energetics for the protonated water clusters. The analysis of Belau et al. has yielded an incremental trimer binding energy of ca. 19.12 kcal/mol, a value that is too high when compared to the results of ab initio electronic structure calculations that yield a value of 7.61 kcal/mol (MP2/Complete Basis Set limit plus harmonic zero-point-energy corrections at the MP2/aug-cc-pVDZ level). Similar discrepancies are also found for the larger clusters. In the present work, we shall show that the relaxation energies in the thermodynamic cycle depicted in Figure 1 are not negligible and therefore their inclusion in the determination of water cluster incremental dissociation energies cannot be neglected.

To show that the zero relaxation assumption is invalid, we rely on the results of ab initio electronic structure calculations at the Møller–Plesset second-order perturbation level of theory<sup>7</sup> (MP2) with the Dunning<sup>8</sup> augmented correlation-consistent polarized valence basis set of double- $\zeta$  quality (aug-cc-pVDZ). The minimum energies for the hydroxyl radical, the neutral<sup>9</sup> and protonated water clusters including harmonic (0 K limit) estimates of the zero-point-energies (ZPEs) are listed in Table 1. We consider the dimer to the hexamer (prism) water clusters in our analysis because the larger water clusters become more complicated due to the existence of many closely spaced energetic minima. Nevertheless, these cluster sizes provide an accurate assessment of the magnitude of the “relaxation”



**Figure 1.** Illustration of the thermodynamic cycle, including relaxation, used to obtain monomer dissociation energies for small neutral water clusters from their measured vertical ionization energies.

**TABLE 1:** Calculated (MP2(full)/aug-cc-pVDZ) Ground State Energies  $E[X]$  and ZPE for the Species  $[X]$  Used in This Study ( $E[X]$  in au and ZPE in kcal/mol)

species $[X]$	$E[X]$	ZPE
$H_2O$	-76.263385	13.39
$(H_2O)_2$	-152.535285	28.91
$(H_2O)_3$	-228.8165515	45.54
$(H_2O)_4$	-305.099954	61.86
$(H_2O)_5$	-381.377942	77.47
$(H_2O)_6$	-457.658913	94.29
$OH\cdot$	-75.567724	5.39
$(H_2O)H^+$	-76.532691	21.66
$(H_2O)_2H^+$	-152.850505	35.57
$(H_2O)_3H^+$	-229.152001	52.30
$(H_2O)_4H^+$	-305.447072	68.15
$(H_2O)_5H^+$	-381.732877	83.36
$(H_2O)_6H^+$	-458.015870	98.01

energies,  $E_n^{\text{relax}}$ . Figure 1 indicates that the inclusion of relaxation in the thermodynamic cycle yields

$$\Delta E_{n+1} = (IE_{n+1} - IE_n) + \Delta E_{n-1}^+ - (E_{n+1}^{\text{relax}} - E_n^{\text{relax}}) \quad (2)$$

where  $E_n^{\text{relax}}$  is the relaxation energy associated with the energy difference between the  $(H_2O)_n^+$  photoionized and “relaxed”  $(H_2O)_{n-1}H^+ + OH\cdot$  asymptotes. These relaxation energies are given by

$$E_n^{\text{relax}} = E[(H_2O)_n^+] - E[(H_2O)_{n-1}H^+] - E[OH\cdot] \quad (3)$$

and the energies of the photoionized levels  $E[(H_2O)_n^+]$  are determined from the measured  $IE_n$ ’s of Belau et al. using the relation

$$E[(H_2O)_n^+] = IE_n + E[(H_2O)_n] \quad (4)$$

**TABLE 2:** Calculated Relaxation Energies  $E_n^{\text{relax}}$  (kcal/mol) Corresponding to the Energy Difference (w/ZPE) between the  $(H_2O)_n^+$  and  $(H_2O)_{n-1}H^+ + OH\cdot$  States as a Function of Cluster Size  $n$

$n$	$E_n^{\text{relax}}$	$\Delta E_{n,n-1}^{\text{relax}} = E_n^{\text{relax}} - E_{n-1}^{\text{relax}}$
1	-137.513	
2	0.163	137.68
3	11.750	11.59
4	17.852	6.10
5	28.327	10.48
6	32.746	4.42

The relaxation energies,  $E_n^{\text{relax}}$ , and their differences,  $\Delta E_{n,n-1}^{\text{relax}} = E_n^{\text{relax}} - E_{n-1}^{\text{relax}}$ , are presented in Table 2. These were calculated using eqs 3 and 4, the ab initio results in Table 1, and the measured  $IE_n$ ’s of Belau et al. The results in Table 2 show that the relaxation energies are quite large. Future work will address the ab initio relaxation dynamics and prediction of IE’s directly.

In summary, we find the relaxation energies to be quite large and therefore they cannot be neglected in the determination of the neutral water monomer dissociation energies. The relaxation energies are significant and the neutral water monomer dissociation energies *cannot* be determined from the experimental IE’s because they are themselves involved in the thermodynamic cycle via eq 4 above.

**Acknowledgment.** We acknowledge Dr. Bruce D. Kay (PNNL) and Dr. Musahid Ahmed (LBNL) for helpful discussions. This work was supported by the Division of Chemical Sciences, Geosciences and Biosciences, Office of Basic Energy Sciences, U.S. Department of Energy. The Pacific Northwest National Laboratory is operated by Battelle for the U.S. Department of Energy. Computer resources were provided by the Office of Science, U.S. Department of Energy.

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