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Heats of Formation of NaOH and NaOH$^+$: Ionization Energy of NaOH

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RCCSD(T) calculations combined with large basis sets are employed to obtain the heats of formation and dissociation energies of NaOH and NaOH$^+$. Our best values are ΔH_f(NaOH,0 K) = −44 ± 1 kcal mol^{-1} and D_0 = 79 ± 1 kcal mol^{-1}. The ground state of NaOH$^+$ is a X$^2\Pi$ state, which is split by a very small Renner−Teller interaction. We calculate AIE (NaOH) = 7.87 ± 0.05 eV, ΔH_f(NaOH$^+$,0 K) = 137 ± 1 kcal mol^{-1}, and D_0 = 16 ± 1 kcal mol^{-1}. The proton affinity of NaO(X$^2\Pi$) is derived as 250 ± 1 kcal mol^{-1}. In addition, we conclude that, experimentally, the vibrational frequencies of neither NaOH nor NaOH$^+$ are known with any reliability.

I. Introduction

The gas-phase alkali metal hydroxides, MOH, are of interest owing to their presence in flames,[1,2] and in particular their involvement in flame inhibition.[3] These species are also involved in the metal chemistry of the Earth's atmosphere.[4] In addition, these species are present in many situations when the alkali metal and water (or steam) come together. Experimental studies on these species are, however, somewhat complicated by the fact that the vapor phase above the MOH(s) contains a number of different species (especially the polymeric species), is highly reactive, and requires a high temperature to obtain a reasonable partial pressure. Accurate modeling of the chemistry of NaOH requires thermochemical data, such as heats of formation and dissociation energies. Similarly, the modeling of the prevalence and chemistry of NaOH$^+$ requires similar data, as well as the ionization energy of NaOH.

A 1986 review by Konings and Cordfunke[5] reports ΔH_f(NaOH,298 K) values of −44.5 ± 2.4 and −47.3 ± 3.1 kcal mol^{-1}, whereas the 1996 review[6] by Gurvich et al. cites −45.6 ± 1.9 kcal mol^{-1} as its recommended value (which is the value cited in a recent compilation[7]). The ΔH_f(NaOH,0 K) value from ref 6 is −44.8 ± 1.9 kcal mol^{-1}. The 1998 JANAF Tables[8] recommend values of ΔH_f(NaOH,298 K) = −47.3 ± 3.0 kcal mol^{-1} and ΔH_f(NaOH,0 K) = −46.4 ± 3.0 kcal mol^{-1}. From the above, it may be seen that there is reasonable agreement for this quantity.

NaOH has been the subject of spectroscopic studies: rotational,[9,10] chemiluminescence,[11] and detection via multiphoton absorption and photofragmentation fluorescence.[12] Theoretical studies have also been undertaken,[13−15] and we shall refer to these below. A more complete summary of the work that has been undertaken on NaOH is contained within ref 6.

Looking at NaOH$^+$, the JANAF[8] Tables recommend a value of ΔH_f(NaOH$^+$,0 K) = 161 ± 25 kcal mol^{-1}, with the value being derived from that of the neutral, combined with an estimate of the ionization energy of NaOH = 9.0 ± 1.0 eV, from Beckett and Cassidy.[16] The JANAF Tables appear to have overlooked the more recent photoelectron work of Dyke, Fehér, and Morris,[17] however. In that work, NaOH was generated by direct heating of the solid to temperatures over 900 K; at temperatures ~700 K, significant amounts of dimer were present, and so higher temperatures were used at which dissociation of these dimers had occurred. This allowed the identification of bands in the photoelectron spectrum as dimer or monomer bands. The monomer band at lowest energy had a maximum at 8.11 ± 0.04 eV, with an onset at 7.68 ± 0.05 eV. ΔSCF calculations, with an approximately double-ζ+ polarization basis set gave an estimate of the vertical ionization energy (VIE) as 8.34 eV, which could be compared, rather favorably, with the maximum in the first photoelectron band. The heat of formation of the cation depends, however, on the adiabatic ionization energy (AIE). This quantity can be determined quite accurately from the onset of a photoelectron band, *if* the ground-state neutral species is cold and if the Franck−Condon factors are high enough. If, however, there is significant vibrational excitation of the neutral molecule, then hot bands may lead to an onset below that of the AIE. If the vibrational structure is fully resolved, then this may not pose a problem; however, the spectra from ref 17 are not well-resolved. Given the relatively high temperatures employed, and on the basis of our recent work on LiOH,[18] LiO,[19] and NaO,[20,21] we expect the AIE of NaOH to be significantly higher than the photoelectron band onset noted above.

In the present work, we perform high-level ab initio calculations on NaOH and NaOH$^+$ to obtain reliable thermochemical properties. We also study the neutral ground electronic state (X$^1\Sigma^+$) and the lowest two cationic states (X$^2\Pi$ and A$^2\Sigma^+$). We note that for NaOH$^+$, a ground-state linear $^2\Pi$ state is expected, which will be subject to a Renner−Teller distortion, and so a breaking of the orbital degeneracy into the A′ and the A″ components.

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TABLE 1: Optimized Bond Lengths (Å), Computed Harmonic Vibrational Frequencies (cm^{-1}), and Total Electronic Energies (E_h, kcal mol^{-1}) for NaOH ($\tilde{X}^1\Sigma^+$)

method	bond lengths	frequencies	E_{tot}
B3LYP[a]	NaO = 1.9424; OH = 0.9524	193π; 567σ; 3970σ	−238.11873
MP2[a]	NaO = 1.9480; OH = 0.9518	265π; 558σ; 4023σ	−237.85732
QCISD[a]	NaO = 1.9426; OH = 0.9490	274π; 565σ; 4040σ	−237.86125
CCSD(T)[a]	NaO = 1.9425; OH = 0.9513	253π; 565σ; 4008σ	−237.87323
CCSD(T)[b]	NaO = 1.9435; OH = 0.9543	275π; 591σ; 3951σ	−237.88132

[a] The 6-311++G(3df,3pd) basis set was used for O and H, and a [6s5p3d1f] basis set for Na (see text for details). [b] The [6s5p3d2f] basis set was used for Na (for details, see text), and the aug-cc-pVTZ basis for O and H was employed.

II. Calculational Details

First, it is important to note that alkali metal compounds are usually ionic, and consequently for NaOH, the basis sets must be capable of describing Na^+ and OH^-. Na^+ also has the interesting feature that the valence 3s orbital of Na is unoccupied in Na^+, and so the $n = 2$ shell effectively becomes the valence shell. We have discussed the basis set demands of Na^+ previously[22] and our basis set design.

Geometries were optimized using MP2, B3LYP, QCISD, and CCSD(T) methods, with unrestricted wave functions being used for the cation. Basis sets used in these optimizations were the 6-311++G(3df,3pd) basis sets for O and H, but for the sodium atoms a [6s5p3d1f] basis set was employed, as follows:

The (27s20p) basis set from Huzinaga[23] was employed, but discarding the six most diffuse s and the six most diffuse p functions. This (21s14p) basis set was then used to perform a Hartree−Fock calculation on Na^+, and the expansion coefficients from this calculation were used to obtain a contracted [2s1p] set of functions, which were selected heuristically to give a good wave function (correct number of nodes, and smooth). To this were added uncontracted functions: four sets of s and p functions with $\zeta = 2.75$, 1.0, 0.3636364, and 0.1322314; three sets of d functions with $\zeta = 2.6$, 0.866667 and 0.288889; and a set of f functions with $\zeta = 1.5$.

The geometries were also optimized employing the (U)-CCSD(T) method, where the standard aug-cc-pVTZ basis sets for O and H were employed, together with a [6s5p3d2f] basis set for sodium, obtained by adding an additional set of f ($\zeta = 0.375$) functions to the [6s5p3d1f] basis set.

In the unrestricted calculations $\langle S^2 \rangle$ was less than 0.76 in all cases, indicating that spin contamination was minimal. All of the above calculations employed the Gaussian[24] suite of programs employing the frozen core approximation, but with only the 1s orbitals on Na and O frozen.

Subsequently, the optimized (U)CCSD(T) geometries obtained using the basis sets noted above were employed in RCCSD(T) calculations using quadruple-ζ and quintuple-ζ basis sets. For H and O, these were the standard aug-cc-pVQZ and aug-cc-pV5Z ones; for Na, the basis sets employed were those we have described previously.[22] We employ the RCCSD(T) procedure,[25] as implemented in MOLPRO;[26] the 1s orbitals on sodium and oxygen were frozen.

III. Results and Discussion

A. Geometry and Vibrational Frequencies of NaOH. The optimized geometries and harmonic vibrational frequencies are given in Table 1. We consider first the vibrational frequencies, which have been studied in matrix isolation experiments.[27] These studies observed infrared absorptions at 431 and 337 cm^{-1}, which were assigned as ν_1 and ν_2, respectively. Note that ν_i implies a fundamental frequency, whereas ω_i implies a harmonic value. The ν_1 value (Na−O stretch) was noted as being less certain, owing to complicated features, probably due to $(\text{NaOH})_n$. CISD calculations by Bauschlicher et al.[28] calculated ω_1 to be 579 cm^{-1} and concluded that the value of ν_1 from ref 27 was probably incorrect. We note that the 579 cm^{-1} value is in good agreement with our best ω_1 value of 591 cm^{-1}, and so agree with the conclusions of Bauschlicher et al. In addition, SCF calculations contained in ref 17 obtained a value of $\omega_1 = 588$ cm^{-1} (note that the numbering scheme is different therein), similar to that obtained in SCF calculations contained in ref 30 of 615 cm^{-1}. We note that very recently Cox and Plane[30] report molecular parameters for NaOH at the CBS-Q level of theory (note that this implies geometry optimization at the MP2/6-31G* level of theory), together with scaled HF/6-31G(d′) frequencies: their values of $\omega_1 = 554$ cm^{-1}, $\omega_2 = 261$ cm^{-1}, and $\omega_3 = 3742$ cm^{-1} are in good agreement with those obtained here and the others cited. The good agreement of all levels of calculations reinforces the conclusions of ref 28.

Our calculated ω_2 value (bending mode) of 275 cm^{-1} is in poor agreement with the SCF value from ref 29, and the value of 431 cm^{-1} from ref 17. Bauschlicher et al. did not report an ω_2 value in ref 28. The matrix isolation value was $\nu_2 = 337$ cm^{-1}, which is far from the value obtained herein. Looking at the spectra reported in ref 27, it can clearly be seen that there were two strong absorptions at 285 and 273 cm^{-1}, which coincide very nicely with the ω_2 value obtained herein. The assignment presented in ref 27 was complicated by the presence of polymeric species: the assignment of bands to NaOH was made on the basis of comparison of spectra at different temperatures, as well as diffusion studies. It is perhaps poignant that the section of the spectrum below ca. 290 cm^{-1} is not shown in some of the spectra, and so the behavior of these two low-frequency bands is unclear; similar comments refer to the region of the spectrum >500 cm^{-1}. Given the level of theory, and our past (and others') experience with these methods, it is highly unlikely that the calculated values are so far from the true values, and we believe the interpretation of the matrix isolation spectra is at fault. The third vibration (O−H stretch) is expected at a frequency >3500 cm^{-1} and does not appear to have been observed directly because of water contamination.[27]

At the MP2 level, we also calculated the isotopic ratios as follows: $\omega_{1,\text{NaOH}}/\omega_{1,\text{NaOD}} = 1.018$; $\omega_{2,\text{NaOH}}/\omega_{2,\text{NaOD}} = 1.325$; $\omega_{3,\text{NaOH}}/\omega_{3,\text{NaOD}} = 1.373$. The ω_2 and ω_3 ratios are close to the value of 1.414 ($=\sqrt{2}$) that one expects for H/D substitution when the motion of H is large; the ω_1 ratio suggests that H is almost motionless during the M−O vibration, as expected. These calculated values are what one expects for the NaOH molecule. The ratios obtained from the matrix isolation study[27] are 1.021 and 1.348, which are very close to the values obtained herein. One possible explanation of the shift of the matrix values from those calculated herein would be a large matrix shift, especially of ω_1, perhaps caused by the ionic nature of the NaOH molecule, leading to a strong interaction with the Ar atoms in the matrix; however, we feel that the shift is too large, and it is more likely that the spectra have been misassigned, and that the peaks

TABLE 2: Optimized Geometrical Parameters (Bond Lengths in Å and Bond Angles in deg), Computed Harmonic Vibrational Frequencies (cm^{-1}), and Total Electronic Energies (E_{tot}, kcal mol^{-1}) of the Low-lying Electronic States[a] of the NaOH$^+$ Cation

method[a]	state	geometry	frequencies	E_{tot}
UB3LYP[b]	$^2\Pi$	NaO = 2.3635; OH = 0.9756	60$i\pi$; 289σ; 433π; 3702σ	−237.89599
UB3LYP[b]	$^2A''$	NaO = 2.2694; OH = 0.9759; NaOH = 165	85a′; 270a′; 3698a′	−237.89600
UQCISD[b]	$^2\Pi$	NaO = 2.2722; OH = 0.9691	55π; 263σ; 440π; 3805σ	−237.58059
UCCSD(T)[b]	$^2\Pi$	NaO = 2.2721; OH = 0.9713	103π; 288σ; 493π; 3777σ	−237.58843
UMP2[b]	$^2\Pi$	NaO = 2.2714; OH = 0.9680	53π; 263σ; 438π; 3832σ	−237.56435
UCCSD(T)[c]	$^2\Pi$	NaO = 2.2675; OH = 0.9739	44π; 291σ; 422π; 3734σ	−237.59459
UCCSD(T)[c,d]	$^2A''$	NaO = 2.2704; OH = 0.9741; NaOH = 167.9	72a′; 265a′; 3729a′	−237.59459
UMP2[b]	$^2\Sigma^+$	NaO = 2.3766; OH = 1.0329	405iπ; 171σ; 3048σ	−237.40246

[a] All calculations are by Gaussian. All correlated calculations had O 1s and Na 1s frozen. All computed $\langle S^2\rangle$ values are ≤0.76. [b] The 6-311++G(3df,3pd) basis set was used for O and H, and a [6s5p3f1d] basis set for Na (see text for details). [c] A [6s5p3d2f] basis set for Na (for details, see text) and the aug-cc-pVTZ basis for O and H was employed. Note that the computed E_h values at the linear and bent optimized geometries are essentially identical. The bending surface is extremely flat. [d] With Opt=tight; same energy as the linear $^2\Pi$ state, suggesting an extremely flat bending surface.

TABLE 3: Computed AIEs and/or [VIEs] (eV) of NaOH at Different Levels of Calculations

method[a]	NaOH$^+$ ($\tilde{\chi}^2\Pi$)[b]	NaOH$^+$ $\tilde{A}^2\Sigma^+$
B3LYP[b]	7.927	
MP2[b]	7.972	12.377[c]
QCISD[b]	7.678	
CCSD(T)[b]	7.750	
RCCSD(T)[d]	7.802	
RCCSD/aug-cc-pVQZ[e]	7.734 [7.965]	[12.505]
RCCSD(T)/aug-cc-pVQZ[e]	7.887 [8.120]	[12.638]
RCCSD/aug-cc-pV5Z[e]	7.753 [7.978]	
RCCSD(T)/aug-cc-pV5Z[e]	7.911 [8.138]	

[a] All calculations are by Gaussian except for RCCSD(T). All correlated calculations had O 1s and Na 1s frozen. All computed $\langle S^2\rangle$ values are ≤0.76. RCCSD(T) calculations were performed by MOLPRO. [b] The 6-311++G(3df,3pd) basis set was used for O and H, and a [6s5p3f1d] basis set for Na (see text for details). [c] This state is a saddle point with the bending mode frequencies being imaginary. See Table 2. [d] A [6s5p3d2f] basis set for Na (for details, see text) and the aug-cc-pVTZ basis for O and H was employed. Note that the computed E_h values at the linear and bent optimized geometries are essentially identical. The bending surface is extremely flat. [e] At the respective CCSD(T)/[6s5p3d2f],aug-cc-pVTZ optimized geometries.

assigned to NaOH probably belong to some other hydrogen-containing molecule. Consequently, any structural information obtained in the matrix study, arising from isotopic shifts in the vibrational frequencies, must be viewed with suspicion.

The bond lengths of NaOH have been estimated[8] as R_{NaO} = 1.93 Å and R_{OH} = 0.97 Å, which are in reasonable agreement with the values obtained herein (Table 1). The estimated values were consistent with a B_0 value of 0.4267 cm^{-1}. Recently[31] the B_0 value has been reported as 0.419 19 cm^{-1} using microwave spectroscopy, which agrees very well with the B_e value calculated herein of 0.422 (QCISD value). The closeness of the microwave and the calculated B values suggests that the calculation is reliable. In addition, the calculated dipole moment at the QCISD level, 6.82 D, agrees extremely well with the experimental value[31] of 6.83 D. The calculated bond lengths agree well also, with the previously obtained values of R_{NaO} = 1.940 Å[13] (CISD), 1.948 Å[14] [CCSD(T)], and 1.951 Å[15] [CCSD(T)].

It is worth noting that the B3LYP geometry is in excellent agreement with the QCISD and CCSD(T) geometries (Table 1). That said, the B3LYP ω_1 vibrational frequency is not in such good agreement. The difference between QCISD and CCSD(T) is not great, although the ω_1 value drops slightly; thus the effect of triples seems to be minimal.

In passing, we note that a benchmark calculation on OH$^-$ has recently appeared,[32] where ω_e was calculated to be 3743 cm^{-1}. The ω_3 frequency of NaOH is essentially an OH$^-$ stretch, but this will be modified from the free OH$^-$ value owing to the small amount of covalency present in the molecule. The R_e(OH$^-$) value of 0.964 Å is in very good agreement with the 0.954 Å value here. Both the R_e and ω_e values are consistent with a small loss of charge from OH$^-$ to Na$^+$, which may be thought of as a donation of electron density from the OH$^-$ π^* orbital, leading to a slightly stronger O−H bond.

B. NaOH$^+$. Table 2 contains the optimized geometries and harmonic vibrational frequencies for NaOH$^+$ calculated at various levels of theory. The first thing to note is that both linear and bent starting structures were employed, and that for the bent structures, $^2A'$ and $^2A''$ states were separately considered. In all cases, the $^2A'$ state became linear and was identical with the results obtained by optimizing the $^2\Pi$ state. At the MP2 and QCISD levels of theory, optimization of the $^2A''$ state also led to a linear structure, identical with the $^2\Pi$ result. A slightly different result was obtained at the B3LYP and CCSD(T) levels of theory, when optimization of the $^2A'$ states again led to linear structures, but the $^2A''$ states optimized to a bent structure. This bent structure was, however, almost isoenergetic with the linear $^2\Pi$ ($^2A'$) state. All of these pieces of information suggest that the Renner−Teller effect is minimal in these molecules, and they are essentially linear, with the barrier to linearity in the $^2A''$ state being almost zero, and so at the zero-point level, the molecule should behave as a linear molecule. Note that the ground state of LiOH$^+$ was concluded to have a more substantial barrier to linearity but was still calculated to be quasilinear.[18] We note that for the calculations carried out here on the $^2\Pi$ state, the π vibrational frequencies were not degenerate, with one of these being quite small in magnitude. This is most likely due to a combination of the presence of a flat saddle point, the inherent inaccuracies of employing numerical second derivatives, and the use of a single-reference method in the QCISD and CCSD(T) calculations.

The position of the first excited $^2\Sigma^+$ state was also calculated herein, and found to be a saddle-point.

Note that no vibrational structure was observed in the photoelectron spectrum,[17] and no other study on the cation appears to have been reported.

C. Ionization Energies. The AIEs and VIEs for NaOH were calculated from energies at the geometries reported in Tables 1 and 2, and the results are given in Table 3. Given the flatness of the cationic surface, we took the linear geometry for the cationic X$^2\Pi$ state. As may be seen, good consistency is obtained, with the best values being AIE = 7.91 eV and VIE = 8.14 eV. Because the ionization of Na$^+$OH$^-$ is essentially the removal of the electron from the OH moiety, it is important to be able to describe the electron affinity well. In addition, any changes in the electron density of the sodium atom also

TABLE 4: Total RCCSD(T)/aug-cc-pV5Z Energies, ZPVEs (kcal mol^{-1}), and Experimental Heats of Formation (kcal mol^{-1})

species	E_{tot}/E_h	ZPVE[a]	ΔH_f(0 K)[a]	species	E_{tot}/E_h	ZPVE[a]	ΔH_f(0 K)[a]
H^+	0.000000	0	365.2 ±0	NaO	−237.198766	1.4[b]	21 ± 2[b]
H	−0.499995	0	51.6 ± 0	NaO^+	−236.920335	0.5[b]	196 ± 2[b]
H_2O	−76.370295	12.9	−57.1 ± 0	NaOH	−237.896567	7.3[c]	
OH^-	−75.737163	5.3	−32.8 ± 0.9	$NaOH^+$	−237.605848	6.4[c]	
Na	−162.096914	0	25.7 ± 0.2	OH	−75.670412	5.4	9.2
Na^+	−161.908440	0	144.2	O	−75.000408	0	59.0

[a] Values from NIST Webbook except where stated. An error of zero implies that the error is smaller than the number of significant figures employed. [b] From ref 20. [c] From the present work.

TABLE 5: Calculated Thermodynamic Quantities (kcal mol^{-1}) at the RCCSD(T)/aug-cc-pV5Z Level; ΔH Values at 0 K

reaction	ΔE_e^{calc}	ΔZPVE	$\Delta H^{calc} = \Delta E + \Delta$ZPVE	ΔH_f(NaOH)
$NaOH + H \rightarrow Na + H_2O$ (1)	−44.3	5.6	−38.7	−44.2
$NaOH + H^+ \rightarrow Na^+ + H_2O$ (2)	−239.8	5.6	−234.2	−43.8
$NaOH + H_2O \rightarrow Na + 2OH + H$ (3)	206.5	−9.4	197.1	−44.4
$NaOH \rightarrow Na + O + H$ (4)	187.8	−7.3	180.5	−44.2
$NaOH \rightarrow Na^+ + OH^-$ (5)	157.5	−2.0	155.5	−44.1
$NaOH \rightarrow Na + OH$ (6)	81.1	−1.9	79.2	−44.3

needed to be well-described. From the total energies in Table 4, one may calculate the adiabatic electron affinity of OH to be 1.816 eV, and IE(Na) is calculated to be 5.129 eV. Comparison with highly accurate experimental data for these values (vide infra) implies that the total error is ~0.5 kcal mol^{-1}, and so we cite the error on the calculated ionization energies to ±1 kcal mol^{-1} (0.05 eV).

Comparing the AIE value to the photoelectron band onset for NaOH reported in ref 17, we see that its value of 7.68 ± 0.05 eV is slightly lower than, but in reasonable agreement with, the calculated value. This calculated value needs to be adjusted by ca. −0.04 eV to account for zero-point vibrational energy, giving 7.87 eV, slightly improving the agreement. That the experimental value is slightly too low is unsurprising, given that the photoelectron spectrum was recorded at 920 K, and so will be prone to hot bands; indeed, thermochemical calculations at 920 K indicate a thermal contribution of ~0.3 eV, which is consistent with the observed difference between the AIE and the observed photoelectron band onset. Of course, to describe the effects of temperature on the appearance of the photoelectron spectrum quantitatively, a Franck−Condon analysis is required. It is interesting to note that the calculated AIE and experimental band onset values for NaOH are much closer than they were in LiOH.[18] In the latter case, the LiOH was produced from heating LiOH(s) in the presence of water (because decomposition of LiOH occurred), and it may be that reactions in the vapor gave rise to internally excited LiOH—a result that, as noted previously,[18] is in line with our findings for LiO,[33] NaO,[34] and NaO_2,[35] all of which were formed by chemical reaction. Clearly, the potential for large amounts of internal excitation is greater from a chemical reaction than just thermal excitation.

D. Dissociation Energies and Heats of Formation of NaOH. The dissociation energy for NaOH was found by calculating the energy difference between NaOH at its equilibrium geometry and Na^+ and OH^-, with correction for basis set superposition error via the full counterpoise correction. Note that the use of the full counterpoise correction here is justified because the NaOH molecule is highly ionic; for LiOH, which is less ionic, this procedure is less straightforward.[18] Our best value for the calculated dissociation energy to ionic products is 157.5 kcal mol^{-1}, obtained using the quintuple-ζ basis set and the CCSD(T) level of theory. To obtain the dissociation energy to the neutral products, the experimental values, IE(Na) = 5.139 08 eV[8] and EA(OH) = 1.827 67 eV[36,37] were employed. This gave a value of the dissociation energy, D_e = 3.52 eV and a D_0 value of 3.43 eV (79 kcal mol^{-1}), with an error of ~1 kcal mol^{-1}. The latter value is in excellent agreement with the value of 3.38 eV obtained by Jensen[38] and is in good agreement with a slightly earlier value of 3.47 ± 0.09 eV from Cotton and Jenkins.[39] Our value is significantly lower than that of Bauschlicher et al.,[13] who obtained a value of 3.59 eV.

ΔH_f(NaOH,0 K) may be derived straightforwardly from a number of reaction schemes, by making use of the calculated total energies, the zero-point vibrational energies, and heats of formation of the various species involved. In Table 4, we collect together the total energies of the relevant species, together with the zero-point energies, and the heats of formation, as obtained from the JANAF Tables and/or a NIST Webbook.[8] In Table 5 are presented the various reaction schemes employed, together with the calculated heats of reaction, the ZPVE changes, and the derived ΔH_f(0 K) value for NaOH. As may be seen, the consistency of the obtained values is very good, even though some of the reaction schemes involve significant bond breaking and charge separation. This consistency is testimony to the accuracy of the theoretical methods employed. From these values, we cite a ΔH_f(NaOH,0 K) value of −44 ± 1 kcal mol^{-1}, well within the error bars of the recommended values, noted in the Introduction. This value is close to recent theoretical values for ΔH_f^{298}, with Schultz et al.[14] obtaining −46.8 kcal mol^{-1} at the G2[CC](dir,full) level of theory and Burk et al. obtaining a value of −40.2 kcal mol^{-1} at the CCSD(T) level of theory, although only scaled HF/6-31G* frequencies were employed.

E. Dissociation Energies and Heats of Formation of $NaOH^+$. $\Delta H_f(NaOH^+)$ may be most easily derived from the ΔH_f(NaOH) value and the AIE, or (equivalently) from the values in Table 4. A value of $\Delta H_f(NaOH^+,0\ K)$ = 137 kcal mol^{-1} is obtained. The D_e value for dissociation to Na^+ + OH products is derived as 17 kcal mol^{-1}, which converts to a D_0 value of 16 kcal mol^{-1}, again an error of ±1 kcal mol^{-1} is cited.

We note that the proton affinity of NaO is easily derived from the reaction

$$NaO + H^+ \rightarrow NaOH^+ \qquad (7)$$

and yields a value of 250 kcal mol^{-1} with an estimated error of 1 kcal mol^{-1}, which is in fairly good agreement with the most recently evaluated value of 255 kcal mol^{-1}.[40]

We note in passing that our values allow a good determination of the ΔH_r for the following reaction:

$$NaO + H_2O \rightarrow NaOH + OH \qquad (8)$$

which has been studied recently by Cox and Plane.[30] We obtain $\Delta H_r(0\ K) = 1.3$ kcal mol^{-1}, with an error of $\sim$1 kcal mol^{-1}, confirming this reaction to be almost perfectly thermoneutral.

IV. Conclusions

High-level ab initio calculations have allowed the thermochemistry of NaOH and $NaOH^+$ to be calculated with high accuracy. The calculated values narrow the error bar on the ΔH_f value for NaOH and dramatically decrease the error in the $NaOH^+$ value. The calculated AIE is in fairly good agreement with the onset of the photoelectron band of NaOH, with the difference probably due to thermal effects. This was in contrast to the case of LiOH, where the photoelectron band onset was far below the calculated AIE.

The calculated vibrational frequencies herein, together with previous calculations, strongly suggest that the 1969 matrix isolation spectrum has been misassigned. There is clearly room for further experimental work in this area.

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