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Na_2O and Na_2O^+: Thermodynamics and Low-Lying Electronic States

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High-level [up to RCCSD(T)/aug-cc-pV5Z′//RCCSD/aug-cc-pVQZ′] ab initio calculations are performed on Na_2O and Na_2O^+ (where the ′ indicates a nonstandard aug-cc-pVXZ basis set). The electronic ground-state equilibrium geometries are found to be linear in both cases. The heats of formation, $\Delta H_f^{298}(Na_2O)$ and $\Delta H_f^{298}(Na_2O^+)$, are derived, with the recommended values being $\Delta H_f^{298}(Na_2O) = -5.5 \pm 1.0$ kcal mol^{-1} and $\Delta H_f^{298}(Na_2O^+) = 106.7 \pm 0.5$ kcal mol^{-1}, respectively. It is found that large basis sets, the RCCSD(T) method, and appropriate account of basis set superposition error (BSSE) are necessary in order to obtain reliable results. S^{298} for Na_2O and Na_2O^+ are also calculated giving 67 and 63 cal K^{-1} mol^{-1}, respectively. The calculations also yield $\Delta H_a^{298}(Na_2O) = 115.5 \pm 1$ kcal mol^{-1} and $D_0(NaO\cdots Na) = 52 \pm 1$ kcal mol^{-1}. The adiabatic ionization energy of Na_2O is calculated as 4.86 ± 0.02 eV and corresponds to the process $Na_2O^+(X^2\Pi_u) + e^- \leftarrow Na_2O(X^1\Sigma_g^+)$; the corresponding vertical ionization energy is calculated to be 5.00 ± 0.02 eV. The ground state of Na_2O^+ is established as the $^2\Pi_u$ state, with the $A^2\Sigma_u^+$ state lying ca. 0.65 eV above. The low-lying triplet states of Na_2O are briefly considered. The implication of the present results on the mass spectrometry of the vapor above Na_2O is discussed.

I. Introduction

(a) Background. The alkali oxide molecules are of great importance in atmospheric chemistry,[1] energy technology,[2] flame chemistry,[3] and chemical lasers;[4] in addition, sodium-containing compounds have been invoked in the chemistry of comets.[5] Na_2O in particular, is an important high-temperature material, and because of this, its vaporization behavior has been the subject of a number of studies. The conclusion from the earlier studies[6−8] was that Na_2O vaporizes congruently, giving a vapor composed of Na and O_2, with small amounts of NaO, NaO_2, and Na_2O. Up until 1991, the thermodynamics of sodium oxides seemed to be fairly well established, with a recommended set of values having been published in 1984.[9] In 1991, however, Steinberg and Schofield published[10] a reevaluation of the vaporization behavior of Na_2O, which led to modifications to the published data presented in ref 9; this reevaluation was based mainly on the assumption that NaO_2 had a strong $Na\cdot\cdot O_2$ bond, and that NaO_2 therefore formed a major component of the vapor above Na_2O, with its nonobservance in mass spectrometric studies being due to the accessing of dissociative regions of the NaO_2^+ potential energy surface upon ionization. There then followed a paper by Hildenbrand and Lau in 1993[11] that disputed the findings of ref 10, concluding that "...there is no need...to reexamine thermochemical data on [sodium oxides] obtained by mass spectrometry, as suggested by Steinberg and Schofield".

Very recently, we attempted to clarify this picture by calculating the spectroscopy, dissociation energies, and heats of formation of NaO and NaO^+ [12−14] and NaO_2 and NaO_2^+ [15] at very high levels of ab initio theory. The convergence of the calculated properties with level of theory allowed error limits to be placed on the calculated values. Although the values obtained are reliable, they did not allow us to say whether the conclusions of ref 10 or 11 were the more correct as the results regarding NaO_2 agreed better with the conclusions of ref 11, whereas those regarding NaO agreed better with the values reported in ref 10. Our conclusion at the time of writing ref 15 was that "the vaporization behavior of Na_2O is still not understood".

In the present paper we calculate ΔH_f^{298} for Na_2O and Na_2O^+ using a specially designed O basis set, with the Na basis set taken from our previous work.[16] The Na basis set used was designed for Na^+, since we had found that other standard Na basis sets seemed to perform poorly for Na^+-containing compounds; it transpired that this basis set performed well for Na also. The O basis set used here has been designed to be more diffuse than standard basis sets, as we anticipated that the oxygen atom in Na_2O would carry a negative charge $> e$. More details of the oxygen basis set will be presented below.

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(b) ΔH_f^{298}(Na$_2$O)—Previous Work. ΔH_f^{298}(Na$_2$O) was derived as -9.9 ± 0.3 kcal mol^{-1} in ref 7 from an average of second and third law mass spectrometric plots. The recommended value in ref 9 was -7.6 ± 2.0 kcal mol^{-1}, which was based on a modified value of that reported in ref 7, together with two values (-8.6 and -7.6 kcal mol^{-1}) obtained by Norman and Winchell (see footnote c of Table 2 in ref 10). The reevaluation of the vaporization behavior of Na$_2$O in ref 10 led to a modification of ΔH_f^{298}(Na$_2$O) to -8.6 ± 1.9 kcal mol^{-1}. The conclusions of the later ref 11, however, are that the values quoted in ref 9 are the more reliable. Interestingly, Lias et al.[17] quote a value of ΔH_f^{298}(Na$_2$O) $= -6$ kcal mol^{-1}, with the source being quoted as ref 18; however, ref 18 cites ref 8 as the source of the ΔH_f^{298} value used therein, with ref 8 citing -9.1 ± 3.0 kcal mol^{-1}, which is clearly not the same as the value cited in ref 17.

The most recent determination of ΔH_f^{298}(Na$_2$O) is a high-level theoretical study by Radom and co-workers:[19] in that work variants of the (now standard) Gaussian-2 (G2) method[20] are employed, such that various approximations used in the standard method are dropped. At the highest level of theory used in that work, G2[CC](dir,full), a value of -7.05 kcal mol^{-1} was obtained. ["CC" refers to the use of CCSD(T) instead of QCISD(T); "dir" refers to the use of direct QCISD(T)/6-311+G(3df,2p) calculations, rather than relying on adding up the various contributions of correlation and basis set; and "full" refers to the inclusion of all electrons in the correlation procedure.]

(c) ΔH_f^{298}(Na$_2$O$^+$) and the Adiabatic Ionization Energy of Na$_2$O—Previous Work. A value for ΔH_f^{298}(Na$_2$O$^+$) only appears to be available in the compilation of Lias et al.,[17] where a value of 110 kcal mol^{-1} is quoted. This value was obtained via the cited value of ΔH_f^{298}(Na$_2$O) $= -6$ kcal mol^{-1} (questioned above) and a cited ionization energy of 5.06 ± 0.4 eV. The source of the ionization energy is ref 18 and was obtained from photoionization efficiency curves (although 5.06 ± 0.1 eV is quoted in the final Table of ref 18). The value from ref 18 appears to be the most recent (and most precise) determination of the ionization energy of Na$_2$O. It is important to note that the ionization energy measured in ref 18 is not necessarily the adiabatic ionization energy (AIE). Previous determinations of the ionization energy of Na$_2$O are 5.5 ± 0.5 eV[7] and 5.35 eV.[21] Theoretical studies have calculated AIE(Na$_2$O), however, with one of the most recent being that of Elliot and Ahlrichs.[22] Using density functional theory (DFT) methods as well as ab initio approaches, they obtained AIE(Na$_2$O) with the MP2/TZPP result = 4.90 eV, comparable with the best DFT methods obtained therein. This value is clearly in good agreement with the experimental result, although it is not clear if zero-point vibrational energy effects were included. A calculation of the vertical ionization energy of Na$_2$O by Green's function methods has been reported by Zakrzewski et al.,[23] where a value of 5.48 eV was obtained.

As stated above, the aim of the present work is to use high levels of ab initio theory to calculate ΔH_f^{298}(Na$_2$O) and to obtain some estimate of the error of the calculated value. In addition, ΔH_f^{298}(Na$_2$O$^+$) will also be calculated, as will be the first and second adiabatic and vertical ionization energies.

The obtained value for ΔH_f^{298}(Na$_2$O) from the present work, and the previously obtained values for ΔH_f^{298}(NaO) and ΔH_f^{298}(NaO$_2$) will then be used as a basis for discussion of the mass spectrometric results.

Finally, the geometry and vibrational frequencies of the lowest-lying triplet states of Na$_2$O will be calculated.

II. Calculational Details

The optimized geometry and the harmonic vibrational frequencies were calculated using standard basis sets and levels of theory up to QCISD in the first instance. The largest practicable calculation was performed in order to obtain harmonic vibrational frequencies: MP2/6-311+G(3df) for Na$_2$O and UQCISD/6-311+G(2d) for Na$_2$O$^+$. The geometries were further optimized at the RCCSD/aug-cc-pVQZ′ level of theory, and these were used for single-point energy calculations at the RCCSD and RCCSD(T) level, employing aug-cc-pVQZ′ and aug-cc-pV5Z′ basis sets (where the ′ indicates that these basis sets are nonstandard). These latter calculations were performed with basis sets for Na and O designed by ourselves (vide infra). Calculations were performed both using the frozen core (FC) approximation and by correlating all electrons (denoted by "full"); in the present work FC implies the freezing of only the 1s orbitals on all atoms.

Gaussian[24] was used for all calculations except the RCCSD and RCCSD(T) calculations, which were performed using MOLPRO.[25]

Analytic gradient methods were used for all geometry optimizations using the Gaussian suite of programs, with analytic second derivatives being used in all cases, except for the QCISD method, where numerical second derivatives were employed. For the RCCSD optimizations, numerical gradients were used.

(a) Basis Sets. The basis sets used for Na were the ones we derived previously, which are of the same type and size as the standard aug-cc-pVXZ basis sets, but have been optimized for Na$^+$ (see ref 16 for full details), and also perform well for Na.

For O, we anticipated that the basis set would have to be diffuse since the oxygen atom in Na$_2$O is expected to carry a charge of between *e* and 2*e*. We thus designed a basis set that was based on the (20s16p) basis set of Huzinaga and Klubukowski.[26] This basis set was contracted to a [2s1p] basis, based upon the results of a Hartree−Fock calculation on Na$_2$O. Additional s, p, d, f, g, and h functions were then added to this basis set in an even-tempered way. The process was trial and error and involved the optimization of the starting exponent and the ratio such that the lowest energy of O and O$^-$ were obtained at the CISD level, and also the best agreement between the calculated electron affinity of O and the experimental value (vide infra) at the RCCSD(T) level. This led to the following values of [exponent, ratio]:

QZ′ basis set*:* s [1.5, 2.6], p [2.6, 3.5], d [4.0, 3.0], f [2.7, 3.0], and g [1.8, 3.0]

5Z′ basis set: s [1.6, 2.25], p [3.2, 2.72], d [4.0, 2.45], f [4.2, 2.55], g [3.5, 2.8], and h [2.5, 2.778]

A number of each type of function was added such that the overall basis set size matched that of the standard aug-cc-pVXZ basis set. The aug-cc-pVQZ′ basis set may be summarized as [6s5p4d3f2g], with the aug-cc-pV5Z′ basis set being summarized as [7s6p5d4f3g2h].

(b) Thermodynamics. Standard formulas were used for the calculation of thermodynamic quantities via statistical mechanics. The rigid-rotor, harmonic oscillator approximation was used throughout: this will lead to small errors, but they are generally found to be minimal (<0.5 kcal mol^{-1}). Rotations and translations were treated classically.

ΔH_f^{298}(Na$_2$O) and ΔH_f^{298}(Na$_2$O$^+$) were calculated via a number of reactions. The total energy change was calculated ab initio, and the thermal corrections were then made (including the zero point vibrational energies) in order to convert these

TABLE 1: Calculated Geometry and Harmonic Vibrational Frequencies of Na_2O ($X^1\Sigma_g^+$)

method	r/Å	$\omega_1(\sigma_g)$/cm^{-1}	$\omega_2(\pi_u)$/cm^{-1}	$\omega_3(\sigma_u)$/cm^{-1}	energy/E_h
MP2(full)/6-311+G(2d)[a]	2.027 $\theta = 157.7°$	345.3	40.7	632.7	−399.108199
MP2(full)/6-311+G(3df)	2.012	335.5	34.8	643.6	−399.172189
B3LYP/6-311+G(2d)	1.987	355.5	67.2	680.0	−399.839673
B3LYP/6-311+G(3df)	1.980	358.1	69.1	684.8	−399.842049
QCISD(full)/6-31+G*	2.048				−398.759481
QCISD(full)/6-311+G(2d)	2.011				−399.101791
RCCSD(full)/aug-cc-pVQZ′	1.970				−399.428299

[a] Note that the geometry calculated at this level of theory is bent, and so the σ and π designations for the vibrational frequencies does not hold—the meaning is obvious, however.

TABLE 2: Calculated Geometry and Harmonic Vibrational Frequencies of Na_2O^+($X^2\Pi$)

method	r/Å	$\omega_1(\sigma_g)$/cm^{-1}	$\omega_2(\pi_u)$/cm^{-1}	$\omega_3(\sigma_u)$/cm^{-1}	energy/E_h [$\langle S^2\rangle$]
UMP2(full)/6-311+G(2d)	2.150	265.0	100.4/130.6	502.7	−398.926233 [0.758]
UMP2(full)/6-311+G(3df)	2.138	264.7	96.7/127.5	501.4	−398.983814 [0.758]
UQCISD(full)/6-311+G(2d)	2.146	266.8	100.5/130.9	505.8	−398.936607 [0.758]
RCCSD(full)/aug-cc-pVQZ′	2.119				−399.235819 [0.750]

TABLE 3: Calculated Geometry and Harmonic Vibrational Frequencies of Na_2O^+($^2\Sigma_u^+$)

method	r/Å	$\omega_1(\sigma_g)$/cm^{-1}	$\omega_2(\pi_u)$/cm^{-1}	$\omega_3(\sigma_u)$/cm^{-1}	energy/E_h [$\langle S^2\rangle$]
UMP2(full)/6-311+G(2d)	2.087	253.9	61.5	468.4	−398.901633 [0.758]
UB3LYP/6-311+G(2d)	2.072	257.7	73.9	475.1	−399.633892 [0.753]
UQCISD(full)/6-311+G(2d)	2.083	255.9	61.2	471.6	−398.911922 [0.758]
RCCSD(full)/aug-cc-pVQZ′	2.054				−399.212041 [0.750]

into enthalpy changes. Thereafter, standard heats of formation of the other species in the reaction were used in order to derive ΔH_f^{298} for the two species of interest.

Adiabatic ionization energies were calculated by calculating the total energy difference between Na_2O and Na_2O^+ at their respective optimized geometries and then corrected for the zero point vibrational energy. Vertical ionization energies were calculated using the same methodology with the total energy difference being carried out at the optimized geometry of the neutral in both cases; in addition, correction for zero point vibrational energy was made in this case only for the neutral state.

For ionic species, the stationary electron convention was used throughout (see ref 17).

III. Results and Preliminary Discussion

(a) Geometry and Harmonic Vibrational Frequencies. The results of the geometry optimization and harmonic frequency calculations are given in Tables 1 and 2 for Na_2O and Na_2O^+, respectively. Looking at the Na_2O results first, it may be seen that the geometry is fairly well converged with theory. Note that a linear molecule was obtained in all cases except at the lowest level of theory employed, MP2/6-311+G(2d), even when the optimizations were commenced at a bent C_{2v} structure. The ab initio results give a slightly longer bond length than the B3LYP DFT method, a result completely in accord with the work of Elliott and Ahlrichs,[22] with almost identical bond lengths being obtained in the present work. Agreement with the MP2/6-31+G* results of Rehm et al.[27] and the DFT results of Goerke et al.[28] are also obtained. No experimental result appears to be available, but we expect that the RCCSD(full)/aug-cc-pVQZ′ value will be in error by less than 0.01 Å and so report a value of $r_e = 1.97 \pm 0.01$ Å.

The vibrational frequencies of Na_2O do not appear to have been reported previously. Some difficulty in calculating the frequencies numerically via the QCISD method were encountered in the present work, and so only values at the MP2 and B3LYP levels are presented in Table 1. The B3LYP values are a little larger than those obtained at the MP2 level, which is consistent with the tighter bonding evinced by the shorter bond length calculated using the former method. We feel the MP2 values are the more reliable at the present time, since the bond length calculated at the MP2 level is in very good agreement with that obtained at the QCISD level with a similar basis set.

The cation, Na_2O^+, does not appear to have been studied much before. To calculate the AIE, the geometry of Na_2O^+ ought to have been optimized, but no explicit results are quoted in ref 22. The first question that needs to be answered is, what is the ground electronic state? From the molecular orbitals of the neutral, we considered the lowest $^2\Pi_u$ and $^2\Sigma_u^+$ states for the cation. The results in Table 2 are for the $^2\Pi_u$ state, with those in Table 3 being for the $^2\Sigma_u^+$ state. It is clear that the $^2\Pi_u$ state was the lower and is hence the ground state, and at the highest level of theory, the $A^2\Sigma_u^+$ state lies 0.65 eV above this. (The ordering is the same as that indicated by the vertical ionization energies, calculated in ref 23.) The vibrational frequencies for both states are fairly consistent with the different levels of theory. This is true even for the UB3LYP method ($X^2\Pi_u$ state), for which the bond length is a little shorter than for the UMP2 and UQCISD approaches. Note, however, that the significantly shorter bond obtained at the RCCSD(full)/aug-cc-pVQZ′ level indicates that the calculated vibrational frequencies may alter at higher levels of theory, but this is not expected to alter the calculated thermodynamics to a large extent.

It is noteworthy that for both states of Na_2O^+ considered, unrestricted wave functions were employed for the MP2, B3LYP, and QCISD methods; although the amount of spin contamination was small, as evinced by the $\langle S^2\rangle$ values being close to 0.750, the π vibrations suffered some loss of degeneracy. For the thermodynamic calculations, the mean of the two components was taken, with a degeneracy of 2.

(b) Heat of Formation of $Na_2O(X^1\Sigma_g^+)$. In deciding which reactions will lead to the most accurate value for $\Delta H_f^{298}(Na_2O)$, a number of considerations must be borne in mind. Isogyricity and isodesmicity are often quoted as being desirable: that is

TABLE 4: Standard Heats of Formation, Calculated Total Energies, and Calculated Thermal Corrections

species	E_{tot}/E_h [a]	thermal correction/ kcal mol^{-1} [b]	ΔH_f^{298}/kcal mol^{-1}
Na	−162.115979	1.480	25.7[c]
Na^+	−161.927536	1.480	144.1[c]
O	−75.036866	1.480	59.56[c]
O^-	−75.090078	1.480	25.82[c]
NaO	−237.258355	2.920	21.6 ± 1.0[d]
NaO^+	−236.978082	2.706	196.5 ± 1.5[d]
Na_2O	−399.462351	4.982	?
Na_2O^+	−399.283733	4.820	?

[a] Calculated at the RCCSD(T,FC)/aug-cc-pV5Z′//RCCSD/aug-cc-pVQZ′ level of theory. [b] The geometries and harmonic vibrational frequencies used are noted in the text; the RRHO approximation was used. This correction includes the ZPVE, the pV term, and the thermal corrections for translation, rotation, and vibration. [c] From ref 17. [d] From ref 13 and the present work. This has a smaller error range than that of ref 13, based on extra calculations performed here; see text.

the spins, and type of bonds broken and made, should balance on both sides of the equation. The idea is that this minimizes the correlation energy change during the reaction and so minimizes errors in its calculation. For NaO (ref 13) we noted that an important consideration there was to note that NaO is actually largely $Na^+{\cdot}O^-$ at its equilibrium geometry, hence calculating the heat of formation via routes that also led to Na^+ and O^- were likely to be the more accurate; this consideration was noted earlier by Langhoff et al.[29] In the present case, Na_2O has a significant amount of $(Na^+)(O^{2-})(Na^+)$ character, with actual Mulliken population analyses in the present work yielding $(Na^{+0.7})(O^{-1.4})(Na^{+0.7})$. One possibility would be dissociation to $2Na^+ + O^{2-}$; however, O^{2-} is not stable, and so its heat of formation is not known. A compromise would be dissociation to $Na^+ + O^- + Na$, which would be expected to give a reliable result if the ionization energy of Na were well described by the theoretical method used (a similar point was raised in ref 13 regarding the dissociation energy of NaO). The atomization route (that used in ref 19) will be accurate only if the ionization of Na *and* the electron affinity of O are well described. Two other possibilities involving NaO will also be discussed below. We present in Table 4 the calculated total energies at the highest level of theory used, thermal corrections, and standard enthalpies of formation of the relevant species involved in the present work.

We first present a summary of the plus and minus points for four reactions that were used to calculate $\Delta H_f^{298}(Na_2O)$.

$$Na_2O \rightarrow 2Na + O \tag{1}$$

Reaction 1 is the atomization route and is expected to be demanding; however, the atomization route is frequently used in standard (e.g., G2) calculations of enthalpies of formation.[30] The differing correlation energy between the two sides of the equation will demand high levels of theory in order to be reliable. In addition, both Na−O bonds are being broken, and the individual spins change. At the very least, reliability for this reaction will demand that the ionization energy of Na and the electron affinity of O be well described.

$$Na_2O \rightarrow Na^+ + Na + O^- \tag{2}$$

Reaction 2 has the advantage over reaction 1 in that the correlation energy on each side of the equation should be more equal since two of the products (Na^+, O^-) are more like the component species of Na_2O. It still requires that the ionization energy of Na be well described, however. In addition, the bonds are still being broken, but since the molecule is quite ionic, this should not lead to a large error.

TABLE 5: Calculated Ionization Energy of Na and Electron Affinity of O

level of theory[a]	IE(Na)/eV	EA(O)/eV
RCCSD(FC)/QZ′	4.88	1.267
RCCSD(full)/QZ′	4.887	1.268
RCCSD(T,FC)/QZ′	4.900	1.425
RCCSD(T,full)/QZ′	4.899	1.428
RCCSD(FC)/5Z′	5.118	1.283
RCCSD(full)/5Z′	5.117	1.284
RCCSD(T,FC)/5Z′	5.129	1.445
RCCSD(T,full)/5Z′	5.128	1.448

[a] FC implies that only the 1s orbital on each atom was frozen.

$$Na_2O \rightarrow NaO + Na \tag{3}$$

In reaction 3, only one bond is being broken and the ionization energy of Na needs to be well described. This route should give an answer comparable to that of reaction 2.

$$Na_2O + O \rightarrow 2NaO \tag{4}$$

In reaction 4, isodesmicity is satisfied. The electron affinity of O is required to be described accurately, and an NaO bond is being broken and made.

If the atomic charges on either side of the reaction are different, then it is expected that the correlation energy will be different, and hence that an error in the calculated energy change (and hence enthalpy) will occur. To gauge the accuracy of our results, we calculated the ionization energy of Na, and the electron affinity of O at all levels of theory used in the present work (Table 5). At the highest level of theory used, RCCSD(T,FC)/aug-cc-pV5Z′, IE(Na) = 5.129 eV, which compares with the experimental value[17] of 5.139 eV. (It is this accurate calculation of IE(Na) that indicates that the basis set is performing well for Na as well as Na^+.) The electron affinity of O was calculated as 1.448 eV, which compares with the experimental value[17] of 1.461 eV. It is clear from Table 5 that the ionization energy of Na is converging faster than the electron affinity of O. At the highest levels of theory, the error in calculating the ionization energy of Na is just smaller than the error in the calculation of the electron affinity of O.

We conclude that reaction 2 should give the most accurate value for $\Delta H_f^{298}(Na_2O)$ on the grounds that the ionization energy of Na is easier to describe than the electron affinity of O; reaction 3 should also give a reliable value. Reactions 1 and 4 are least likely to lead to a reliable value for $\Delta H_f^{298}(Na_2O)$ since they rely on the accurate calculation of the electron affinity of O; however, the errors from these effects should be small (vide infra).

(i) Errors Arising from Basis Set Superposition Error (BSSE). One major difficulty in any ab initio calculation is the presence of BSSE. The usual place where this arises is when two moieties are interacting weakly; in such circumstances some ghost center calculation is performed, such as the full counterpoise method, and the BSSE is subtracted from the calculated interaction energy. In principle, BSSE is present in all molecules in a conventional ab initio calculation to some extent when a finite basis set is employed, and the problem arises as to how to correct for it. When a molecule is very ionic, this becomes quite straightforward. For example, in our calculations[13] on NaO, we corrected for BSSE by considering the molecule as an interaction between Na^+ and O^-, a reasonable approximation. Similarly for CaF_2, we were able to consider the molecule as an interaction

TABLE 6: Calculated $\Delta H_f^{298}(Na_2O)$ at Various Levels of Theory

level of theory[a]	calculated $\Delta H_f^{298}(Na_2O)$/kcal mol^{-1} reaction 1	reaction 2	reaction 3	reaction 4
	No BSSE Correction			
RCCSD(FC)/QZ′	−6.41	−5.25		−2.12
RCCSD(full)/QZ′	−7.62	−6.42		−2.13
RCCSD(T,FC)/QZ′	−15.91	−11.39		−5.54
RCCSD(T,full)/QZ′	−17.23	−12.62		−5.56
RCCSD(FC)/5Z′	+2.86	−0.92	+0.58	−1.70
RCCSD(full)/5Z′	+0.09	−3.65	−0.54	−1.17
RCCSD(T,FC)/5Z′	−7.04	−7.34	−6.16	−5.28
RCCSD(T,full)/5Z′	−9.94	−10.13	−7.35	−4.76
	Including BSSE Correction			
RCCSD(FC)/QZ′	−4.93	−3.77		
RCSD(full)/QZ′	−5.11	−3.91		
RCCSD(T,FC)/QZ′	−14.32	−9.80		
RCCSD(T,full)/QZ′	−14.64	−10.60		
RCCSD(FC)/5Z′	+4.67	+0.89	+1.60	
RCCSD(full)/5Z′	+4.43	+0.69	+1.45	
RCCSD(T,FC)/5Z′	−5.10	−5.40	−5.11	
RCCSD(T,full)/5Z′	−5.47	−5.66	−5.32	

[a] FC implies that only the 1s orbital on each atom was frozen.

between two F^- and Ca^{2+}.[31] In the present case, things are not so simple. Na_2O might be approximated as having two Na^+, but the oxygen atom (which carries a charge of $-1.4e$) can only reasonably be approximated as O^-. This selection of fragments to calculate BSSE is a general problem for covalently bonded species, and one of us has discussed this elsewhere.[32]

For reactions 1 and 2, the question arises as to what fragments to use to correct for BSSE. For reactions 1 and 2 we initially considered the appropriate products in the ghost center calculations; however, the resulting $\Delta H_f^{298}(Na_2O)$ between the two reactions was not consistent. It emerged that in both cases only ionic fragments should be used in the ghost center calculations since these are more like the constituent fragments in Na_2O at its equilibrium geometry. This procedure is then more in the spirit of Boys and Bernardi's original recipe,[33] which suggested that the counterpoise correction should be performed, keeping everything as close as possible to the character of the equilibrium species. (Strictly, fractional charges on the atomic fragments should be used in the counterpoise correction; however, this is impractical; in addition, it would appear that the overestimate of the charge on Na and the underestimate of the charge on O during the counterpoise correction should balance somewhat.) This procedure is also more logical as the BSSE arises from the constituent fragments of the molecule by attempting to lower their energy, and in the molecule, they are highly ionic. For reaction 3, the BSSE was calculated by using $(NaO)^GNa^+$ and $NaO(Na)^G$ as the fragments, where the G indicates a ghost center.

Finally, we felt that a reliable BSSE correction for reaction 4 was not possible, but we anticipated that this would be small as both sides of the reaction are similar from a BSSE point of view.

It may be seen from the calculated $\Delta H_f^{298}(Na_2O)$, presented in Table 6, that it is only when BSSE has been accounted for that a consistent picture emerges, with the values at the RCCSD(T)/aug-cc-pV5Z′ level of theory being very similar from reactions 1−3; additionally, reaction 4 (uncorrected for BSSE) leads to values that are not too dissimilar.

(ii) Errors Due to Charge Change. By noting the difference between the calculated ionization energy of Na and the electron affinity of O, and the experimental values, it is possible to estimate the error in the calculated ΔH_f^{298}. Thus, at the RCCSD(T,full)/aug-cc-pV5Z′ level of theory, the expected error in $\Delta H_f^{298}(Na_2O)$ from reaction 1 is 0.033 eV (0.76 kcal mol^{-1}), for reaction 2 is 0.01 eV (0.23 kcal mol^{-1}), and from reaction 3 is 0.01 eV (0.23 kcal mol^{-1}). We disregard reaction 4, since the BSSE has not been corrected.

TABLE 7: Calculated $\Delta H_f^{298}(Na_2O^+)$ at Various Level of Theory

level of theory[a]	calculated $\Delta H_f^{298}(Na_2O^+)$/kcal mol^{-1} reaction 5	reaction 6	reaction 7
	No BSSE Correction		
RCCSD(FC)/QZ′	104.8	103.4	105.7
RCCSD(full)/QZ′	103.7	102.5	105.2
RCCSD(T,FC)/QZ′	105.5	101.0	106.2
RCCSD(T,full)/QZ′	104.4	99.8	105.7
RCCSD(FC)/5Z′	103.9	107.6	105.4
RCCSD(full)/5Z′	101.2	105.0	104.4
RCCSD(T,FC)/5Z′	104.2	104.9	105.8
RCCSD(T,full)/5Z′	101.9	102.1	104.7
	Including BSSE Correction		
RCCSD(FC)/QZ′	106.2	105.1	
RCCSD(full)/QZ′	106.2	105.0	
RCCSD(T,FC)/QZ′	107.1	102.5	
RCCSD(T,full)/QZ′	107.0	102.4	
RCCSD(FC)/5Z′	105.7	109.5	106.4
RCCSD(full)/5Z′	105.6	109.3	106.4
RCCSD(T,FC)/5Z′	106.6	106.9	106.9
RCCSD(T,full)/5Z′	106.4	106.6	106.7

[a] FC implies that only the 1s orbital on each atom was frozen.

(c) Heat of Formation of Na_2O^+. A similar approach was taken to determine $\Delta H_f^{298}(Na_2O^+)$. The reactions considered were

$$Na_2O^+ \rightarrow 2Na^+ + O^- \tag{5}$$

$$Na_2O^+ \rightarrow Na^+ + Na + O \tag{6}$$

$$Na_2O^+ \rightarrow NaO + Na^+ \tag{7}$$

The calculated $\Delta H_f^{298}(Na_2O^+)$ values, with and without BSSE correction (performed in an identical manner to the Na_2O calculations), are given in Table 7. It is immediately apparent that the calculated ΔH_f^{298} values are much more consistent than in the case of Na_2O. But, as before, the values after correction for BSSE are more consistent than those before correction. As with Na_2O, we can estimate the error arising as a result of errors in the calculation of the ionization energy of Na and the electron affinity of O. At the highest level of theory, RCCSD(T,full)/aug-cc-pV5Z′, these errors are 0 eV (0 kcal mol^{-1}), 0.023 eV (0.53 kcal mol^{-1}), and 0 eV (0 kcal mol^{-1}) for reactions 5−7, respectively.

(d) Ionization Energies. *(i) $Na_2O^+(X^2\Pi_u) + e^- \leftarrow Na_2O(X^1\Sigma_g^+)$.* The process

$$Na_2O^+(X^2\Pi_u) + e^- \leftarrow Na_2O(X^1\Sigma_g^+) \tag{8}$$

is the lowest energy ionization of Na_2O. A simple subtraction of the calculated total energies for the two species involved and a correction for the ZPVE leads to the AIE. The results are shown in Table 8, and it is immediately apparent that the basis set effect is close to saturation, as adjudged by the fact that the QZ′ and 5Z′ basis sets lead to almost identical results, for a corresponding level of theory. In addition, freezing the 1s orbitals or otherwise makes only a very small difference. The BSSE in Na_2O^+ and Na_2O is likely to be similar, and so the

TABLE 8: Calculated First AIE (eV) of Na_2O at Various Levels of Theory $Na_2O^+(X^2\Pi_u) + e^- \leftarrow Na_2O(X^1\Sigma_g^+)$

level of theory[a]	AIE[b]
RCCSD(FC)/QZ′	4.531 (4.527)
RCCSD(full)/QZ′	4.533 (4.529)
RCCSD(T,FC)/QZ′	4.843 (4.839)
RCCSD(T,full)/QZ′	4.848 (4.844)
RCCSD(FC)/5Z′	4.535 (4.531)
RCCSD(full)/5Z′	4.539 (4.535)
RCCSD(T,FC)/5Z′	4.857 (4.853)
RCCSD(T,full)/5Z′	4.860 (4.856)

[a] FC implies that only the 1s orbital on each atom was frozen. [b] The values in parentheses include the ΔZPVE calculated at the (U)MP2/6-311+G(3df) level of theory. ZPVE(Na_2O) = 0.065 eV; ZPVE(Na_2O) = 0.061 eV.

only significant error is likely to arise as a result of the charge change upon ionization. As noted above, Na_2O has a charge distribution $Na^{+0.7}O^{-1.4}Na^{+0.7}$ and Na_2O^+ has a distribution, $Na^{+0.9}O^{-0.8}Na^{+0.9}$. Considering the errors in charge changes noted above, this error is unlikely to exceed 0.02 eV, and so we quote a recommended value for the AIE of 4.86 ± 0.02 eV.

(ii) $Na_2O^+(A^2\Sigma_u^+) + e^- \leftarrow Na_2O$ and Some Remarks on the Photoelectron Spectrum of Na_2O. Table 3 contains the calculated equilibrium geometry and harmonic vibrational frequencies for $Na_2O^+(A^2\Sigma_u^+)$. We calculate the AIE corresponding to the process

$$Na_2O^+(A^2\Sigma_u^+) + e^- \leftarrow Na_2O(X^1\Sigma_g^+) \qquad (9)$$

at the RCCSD(T)/aug-cc-pVQZ′ level of theory, with the frozen core (FC) approximation. This yielded a value of 5.492 eV, converting to 5.480 after correction for ZPVE. We expect this value to change little if all electrons had been correlated, or if the 5Z′ basis set had been used (see the calculated AIEs in Table 8).

For both the $X^2\Pi_u$ state and the $A^2\Sigma_u^+$ state, we calculated the VIE at the RCCSD(T,FC)/aug-cc-pVQZ′ level of theory, yielding values of 5.031 and 5.545 eV, respectively; correction for ZPVE yields 4.966 and 5.493 eV, respectively.

Consideration of the symmetric stretch frequencies in both cases, coupled with the difference between the AIE and the VIE, suggests that both the first and second bands of the photoelectron spectrum of Na_2O will have a small number of vibrational components.

(e) Recommended Values for $\Delta H_f^{298}(Na_2O)$ and $\Delta H_f^{298}(Na_2O^+)$. It is important to note that rather than extending our results to basis set completion, we argue the reliability of the results on the grounds of close agreement via different routes, which contain different demands from the basis sets, different reliance on the accuracy of electron correlation description, and different BSSE effects. We have attempted also to quantify the reliability of the results by computing EA(O) and IE(Na) and show that at the highest level of theory close agreement is obtained; however, in Na_2O itself, fractional charges are involved, and this comparison is not totally justified. We reiterate, however, that the $<+1e$ charge on Na and the $<-2e$ charge on O will lead to a cancelation of errors to some extent. In principle, it is possible to increase the basis set further and look for convergence; however, this becomes very expensive—the convergence of the two quantities, IE(Na) and EA(O^-), at the highest level of theory used here, is taken to imply near-convergence of the other properties calculated herein. Another possibility would be extrapolation: in the cases of AIE(Na_2O) and $\Delta H_f^{298}(Na_2O^+)$, convergence is obtained, so that any extrapolation technique will lead to essentially the same values; thus, for $\Delta H_f^{298}(Na_2O)$, essentially the same value will be obtained.

Looking at the results contained in Tables 6−8, it may be seen that the AIE is the most consistent value calculated, with the difference between the QZ′ and 5Z′ results being <0.02 eV. The effect of taking some account of triple excitations increases the AIE by 0.3 eV, with this effect being more or less constant at the various levels of theory used. As discussed above, owing to the accuracy of our calculation of IE(Na) and EA(O), we quote an accuracy of 0.02 eV for AIE(Na_2O).

Looking now at $\Delta H_f^{298}(Na_2O^+)$ from Table 7, we see that at the highest level of theory, after BSSE correction, we obtain a set of three highly consistent values for ΔH_f^{298} from reactions 5−7, with the difference being <0.3 kcal mol^{-1}. Comparing with the QZ′ values, we see that change between QZ′ and 5Z′ is <3 kcal mol^{-1}, with the major difference being the value from reaction 6, which requires the IE(Na) and EA(O) to be described accurately. From the discussion above, it is clear that the required accuracy for these processes only occurs at the 5Z′ level of theory, where the errors are very small. Thus, we are confident that the 5Z′ values (after correction for BSSE) are reliable for $\Delta H_f^{298}(Na_2O)^+$ and that the error should not exceed 0.5 kcal mol^{-1}. We quote a recommended value of $\Delta H_f^{298}(Na_2O^+) = 106.7 \pm 0.5$ kcal mol^{-1}.

Now, using the AIE and the value for $\Delta H_f^{298}(Na_2O)$ allows us to calculate $\Delta H_f^{298}(Na_2O)$, taking account of the thermal corrections. This procedure leads to $\Delta H_f^{298}(Na_2O) = -5.2 \pm 0.7$ kcal mol^{-1}. Looking now at the values of $\Delta H_f^{298}(Na_2O)$ derived from reactions 1−4 in Table 6, it may be seen that a consistent picture only emerges at the highest level of theory, with the results at the QZ′ level, and also those ignoring triple excitations being significantly removed from the final values. One might, on the basis of these values alone, question the convergence of those final values. However, there are other indicators. First, the calculated IE(Na) and EA(O) suggest that it is only at the highest level of theory that these quantities are reliably calculated, and of course, these are highly related to the processes occurring in reaction 1−4. Also, the BSSE is clearly playing a role, and it is when this is corrected that a consistent set of values is obtained. Finally, and perhaps most importantly, the final set of (three) values in Table 6 agree with each other (to within 0.4 kcal mol^{-1}), and also with the value of $\Delta H_f^{298}(Na_2O)$ obtained via (probably the most reliable route) the AIE and $\Delta H_f^{298}(Na_2O^+)$ above. Taking all of these points into consideration, we feel that a final recommended value of $\Delta H_f^{298}(Na_2O) = -5.5 \pm 1$ kcal mol^{-1} is justified, where the error has been rounded to the nearest 0.5 kcal mol^{-1}.

(f) Atomization Energy of Na_2O [$\Delta H_a^{298}(Na_2O)$] and D_0(NaO···Na). From the calculated ΔH_r^{298} of reactions 1 and 3, we were able to obtain $\Delta H_a^{298}(Na_2O)$ directly, and derive D_0(NaO···Na).

$\Delta H_a^{298}(Na_2O)$ was evaluated as 115.5 ± 1 kcal mol^{-1}, which is calculated at the RCCSD(T,full)/aug-cc-pV5Z′ level of theory, after having been corrected for BSSE and thermal effects; the error (corrected up to 1 kcal mol^{-1}) arises as a result of charge changes during the reaction.

D_e(NaO···Na) was calculated as 52.9 kcal mol^{-1}, which converts to $D_0 = 52 \pm 1$ kcal mol^{-1}, where again, the error has been corrected up to 1 kcal mol^{-1}.

These two values are in reasonable agreement with earlier values summarized in ref 7, and with the values obtained therein [$\Delta H_a^{298}(Na_2O) = 121.1 \pm 3$ kcal mol^{-1} and D_0(NaO···Na) = 60.3 ± 4 kcal mol^{-1}], but are slightly lower in both cases. The calculated D_0 value may be compared to values of 58 ± 2 kcal mol^{-1} [9] and 54.5 ± 2 kcal mol^{-1},[10] where the agreement can be seen to be good.

TABLE 9: Calculated Equilibrium Geometry and Harmonic Vibrational Frequencies for the Lowest-Lying Triplet States of Na_2O[a]

level of theory	r_e/Å	θ/deg	ω_1/cm^{-1} ($\sigma g/a_1$) sym str	ω_2/cm^{-1} (π_u/a_1) bend	ω_3/cm^{-1} (σ_u/b_2) asym str	energy/E_h [$\langle S^2\rangle$]
Linear $^3\mathbf{\Pi_u}$ ($\cdots\sigma_u^2\pi_u^3\sigma_g^1\sigma_u^0$); ($\cdots b_2^2b_1^1a_1^2a_1^1b_2^0$) ã $^3\mathbf{B_1}$ Bent						
UB3LYP	2.170	103.1	351.5	79.1	379.1	−399.806704 [2.004]
UMP2(full)	2.184	95.6	362.7	115.6	365.8	−399.055802 [2.002]
UQCISD(full)	2.180	95.6	365.8	115.8	368.5	−399.067866[2.008]
Linear $^3\mathbf{\Pi_u}$ ($\cdots\sigma_u^2\pi_u^3\sigma_g^1\sigma_u^0$); ($\cdots b_2^2b_1^1a_1^2a_1^1b_2^0$) $^3\mathbf{A_1}$ Bent						
UMP2(full)	2.139	107.7	363.5	84.2	386.2	−399.050551 [2.008]
UQCISD(full)	2.135	107.9	*b*	*b*	*b*	−399.062566 [2.008]
Linear $^3\Sigma_\mathbf{u}^+$ ($\cdots\sigma_u^1\pi_u^4\sigma_g^1\sigma_u^0$); ($\cdots b_2^1b_1^2a_1^2a_1^1b_2^0$) $^3\mathbf{B_2}$ Bent						
UMP2(full)	2.181	87.2	331.3	149.7	350.7	−399.043302 [2.008]
Linear $^3\mathbf{\Pi_g}$ ($\cdots\sigma_u^2\pi_u^3\sigma_g^0\sigma_u^1$); ($\cdots b_2^2b_1^2a_1^1a_1^0b_2^1$) $^3\mathbf{B_2}$ Bent						
UMP2(full)	2.165	170.0	257.5	98.3/99.3	545.7	−399.035869 [2.008]
UQCISD(full)	2.166	180.0	254.2	65.0/100.8	553.0	−399.047967 [2.008]
Linear $^3\mathbf{\Pi_g}$ ($\cdots\sigma_u^2\pi_u^3\sigma_g^0\sigma_u^1$); ($\cdots b_2^2b_1^1a_1^2a_1^0b_2^1$) $^3\mathbf{A_2}$ Bent						
UMP2(full)	2.168	165.2	258.4	65.8/68.4	541.5	−399.035890 [2.008]
Linear $^3\mathbf{\Sigma_g}^+$ ($\cdots\sigma_u^1\pi_u^4\sigma_g^0\sigma_u^1$); ($\cdots b_2^1b_1^2a_1^2a_1^0b_2^1$) $^3\mathbf{A_1}$ Bent						
UMP2(full)	2.108	170.8	242.6	$-27.4i$[c]	564.9	−399.015328 [2.008]

[a] 6-311+G(2d) basis set used in all cases. For the C_{2v} designations, the molecule lies in the *yz* plane. [b] Numerical frequency calculation led to problems. [c] We did not attempt to converge the geometry of this state tightly; we believe that it is a very shallow potential energy surface along the bending direction.

(g) Calculated Entropies. It is straightforward to calculate the standard molar entropies once the equilibrium geometry (and so rotational constants) and harmonic vibrational frequencies have been obtained. As with the thermal corrections, the harmonic vibrational frequencies at the (U)MP2/6-311+G(3df) level were used. The values obtained in the present work are 67 cal K^{-1} mol^{-1} for Na_2O and 63 cal K^{-1} mol^{-1} for Na_2O^+. For Na_2O, an estimated value has been reported by Lamoreaux and Hildenbrand[9] of 62.3 ± 1.5 cal K^{-1} mol^{-1}, which is close to the value obtained here. The estimated value[9] had to assume the geometry and values for the harmonic vibrational frequencies, which would have led to small errors in those values: thus, the two values are in good agreement.

(h) Low-Lying Triplet States of Na_2O. The lowest-lying triplet states of Na_2O were also studied. In all cases, the charge distribution was calculated to be approximately $Na^{+0.35}O^{-0.7}Na^{+0.35}$, which corresponds to the fact that these are all charge-transfer states, with an electron from oxygen being excited onto the Na atoms.

The optimized geometries and harmonic vibrational frequencies are presented in Table 9. (For the purposes of this discussion, the C_{2v} point group is considered, with the *yz* plane being that of the molecule.) As may be seen, unrestricted wave functions were used, and the amount of spin contamination was small, with $\langle S^2\rangle$ being very close to the theoretical 2.000. The lowest state is the ã $^3B_1$ (...$b_1^1a_1^1$) state, with a $^3A_1$ (...$a_1^1a_1^1$) lying above. (At the UQCISD/6-311+G(2d) level of theory, the separation (T_e) is 0.14 eV ($^3A_1 \leftarrow {}^3B_1$); the $^3B_1$ state lies 0.92 eV above the $\tilde{X}$ $^1\Sigma_g^+$ state.) Both the $^3B_1$ and the $^3A_1$ states are clearly bent and are the two Renner−Teller components of a linear $^3\Pi_u$ state. These two states arise from excitation of a π_u electron (essentially the lone pairs of the O atom) to the σ_g orbital, which arises from the bonding combination of the two 3s Na orbitals. These states are bent to allow maximum overlap between the two 3s orbitals. About 0.18 eV above lies a $^3B_2$ state, which is also found to be highly bent. It arises as a result of excitation from the in-plane p_x orbital on oxygen to the bonding combination of Na 3s orbitals. Again, the bending results as the two Na 3s orbitals attempt to maximize their overlap. This state correlates to a $^3\Sigma_u^+$ state in a linear orientation.

Next highest in energy are the two components of a $^3\Pi_g$ state ($^3B_2$ and $^3A_2$), which arises from excitation from the two lone pair orbitals on oxygen to the antibonding combination of Na 3s orbitals. Now the molecule attempts to stay linear, since this will minimize the overlap between the 3s orbitals; however, the Renner−Teller effect occurs, which leads to a small bending of each state. Note that these two components are very close in energy, and really they correspond to a quasilinear $^3\Pi_g$ state. This quasilinearity is also displayed by the bending mode (π_u/a_1), which actually has a large component as part of the rotations; this is included as one of the bending vibrations in Table 9, since in the limit of linearity, this is what it will become.

Finally, the highest energy state considered is a $^3A_1$ state, which is close to linearity (at linearity, this state is a $^3\Sigma_g^+$ state). It arises from excitation of one of the in-plane O p_x electrons to the antibonding combination of Na 3s orbitals, which explains its near linearity.

IV. Further Discussion

(a) $\Delta H_f^{298}(Na_2O)$ and $\Delta H_f^{298}(Na_2O^+)$. The present work presents an attempt at calculating the most accurate value of $\Delta H_f^{298}(Na_2O)$. Of particular note is that correlating all electrons (full) leads to much more negative values of $\Delta H_f^{298}(Na_2O)$, the explanation for this is due to core BSSE effects (i.e., the core orbitals are using the ghost center orbitals to lower their energy). This effect was almost completely eradicated by the full counterpoise correction, as evinced by the closeness of the FC and full results after BSSE correction (bottom half of Table 6). Our value at the RCCSD(T,FC)/aug-cc-pV5Z′ level from reaction 1, *before* counterpoise correction, is almost identical to that obtained in ref 19, which must be in some part fortuitous, as the basis set used in ref 19 was smaller than that used herein; but BSSE is affecting both of these values, and its correction here leads to a value 1.5 kcal mol^{-1} less negative. It is also apparent from Table 6 that the highest levels of theory are required to obtained reliable energetics for this system. As we noted above, we believe this is due to the necessity of being able to describe the charge changes that occur during the reactions used to calculate $\Delta H_f^{298}(Na_2O)$, and the requirements

TABLE 10: Recommended Values of ΔH_f^{298} for NaO($X^2\Pi$), $NaO_2(\tilde{X}^2A_2)$, and $Na_2O(X^1\Sigma_g^+)$

	mass spectrometry	recent calculations
NaO($X^2\Pi$)	25 ± 1^a	22 ± 1^c
	21 ± 1^b	
$NaO_2(\tilde{X}^2A_2)$	$\geq -2^a$	-13 ± 3^d
	-33 ± 2^b	
Na_2O ($X^1\Sigma_g^+$)	-8 ± 2^a	-7.04^e
	-9 ± 2^b	-5.5 ± 1.0^f

[a] From ref 9. [b] From ref 10. [c] From ref 13 and additional calculations performed in this work. See text for details. [d] From ref 15. [e] From ref 19. [f] This work.

for the high level of theory required are demonstrated in Table 5. Both a quintuple ζ basis set and account of triple excitations are necessary.

We have confidence in our calculated $\Delta H_f^{298}(Na_2O)$ value since we obtain very similar results using three different reactions (1)−(3) and also when going via the AIE route.

(b) Ionization Energies. Our calculated AIE(Na_2O) agrees very well with the recent calculated value of 4.90 eV by Elliot and Ahlrichs,[22] and with the most recent experimental determination (5.06 ± 0.1 eV) of Peterson et al.[18] Interestingly, our calculated VIE is more or less the same as the position of the sharp onset of the PIE spectrum in that work. Our calculated VIE (5.03 eV) is in rather poor agreement with the value of 5.48 eV reported in ref 23 using Green's function approach; this possibly arises as a result of the small basis set (6-31+G*) used therein.

(c) Relevance to Mass Spectrometric Studies. Table 10 summarizes the recommended thermodynamic quantities from recent mass spectrometric data and calculations. It seems clear that the thermodynamics of NaO($X^2\Pi$) are fairly well-established, with good agreement between the mass spectrometric studies, and our recent high-level ab initio calculations. As noted in ref 13, we are confident of our value there, owing both to the high levels of theory employed, and also because we corrected for BSSE, and judged the performance of the calculations against the calculated ionization energy of Na and the electron affinity of O. We performed additional calculations in the present work using the more diffuse O basis set, and these, coupled with the good agreement between reactions 1−3 for calculating $\Delta H_f^{298}(Na_2O)$, suggest that ΔH_f^{298}(NaO) is 22 ± 1 kcal mol^{-1}, i.e., the same value as obtained previously, but with a narrower error margin.

There is clearly disagreement between the experimentally derived $\Delta H_f^{298}(NaO_2)$ values and our recent calculated value; however, this large disagreement is a little misleading. In the later ref 11 the dissociation energy ($Na\cdots O_2$) rather than ΔH_f^{298} was discussed in relation to the mass spectrometric studies of the vapor above Na_2O. It was concluded therein that the dissociation energy, $D_0(Na\cdots O_2)$, obtained by Steinberg and Schofield[10] (58 ± 2 kcal mol^{-1}) was too high and that a value of ≤43 kcal mol^{-1} was more reasonable. Our recent calculated value[15] (36 ± 3 kcal mol^{-1}) is in good agreement with the upper bound of ref 11 and the previously reported calculations of Partridge et al.[34] Again, we could judge the accuracy by calculating the ionization energy of Na and the electron affinity of O_2 (since NaO_2 is very ionic at its equilibrium geometry, whereas the products of the dissociation are neutral): IE(Na) was calculated as 5.129 eV and the electron affinity of O_2 was calculated as 0.425 eV; comparing these to the respective experimental values of 5.139 and 0.451 eV,[17] we can see that the error arising from charge change effects is <1 kcal mol^{-1}. This, coupled with BSSE corrections, led to the error quoted in ref 15. Thus, our calculated $\Delta H_f^{298}(NaO_2)$ value, which relies on the calculated $D_0(Na\cdots O_2)$ value, must be more consistent with the recent mass spectrometric conclusions.

Finally, regarding $\Delta H_f^{298}(Na_2O)$, our value is a little higher than the recently calculated value (probably due to a mixture of basis set and BSSE effects, with the latter not being considered in ref 19). It is, however, in agreement with the experimental values, once the error ranges have been taken into consideration. Our value could possibly be a little high, owing to the fact the full counterpoise correction might tend to overcorrect BSSE; however, the good agreement between the calculated ΔH_f^{298} via reactions 1−3 (and to some extent, reaction 4), together with agreement via $\Delta H_f^{298}(Na_2O^+)$ and the AIE, lead us to have some confidence in our quoted value.

In summary, we concur with the authors of ref 11 that the reanalysis[10] of earlier mass spectrometric data[7] is in error, mainly on the basis of the NaO_2 results. This suggests, as noted in ref 11, that the vapor above $Na_2O(s)$ is mainly Na and O_2, with minor amounts of Na_2O, NaO_2, and NaO.

V. Conclusions

High-level ab initio calculations were used to derive $\Delta H_f^{298}(Na_2O)$ and $\Delta H_f^{298}(Na_2O^+)$, yielding recommended values of −5.5 ± 1.0 and 106.7 ± 0.5 kcal mol^{-1}, respectively. It was found that high levels of theory and correction for BSSE were necessary in order to obtain consistent values via a number of reaction routes. The AIE was also calculated, yielding a value of 4.86 ± 0.02 eV. The ground state of Na_2O^+ was established as a $^2\Pi_u$ state, with the $A^2\Sigma_u^+$ state lying 0.65 eV above. The appearance of the photoelectron spectrum of Na_2O was briefly discussed.

The lowest-lying triplet states of Na_2O were briefly investigated.

Finally, we conclude that the interpretation of the mass spectrometry of the vapor above $Na_2O(s)$ presented in the original work[7] and rediscussed later[11] is more reliable than a suggested reanalysis.[10] It is important to note this, since even in the light of ref 11, recent mass spectrometric studies[35] refer to the conclusions of ref 10.

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