Spectroscopy and Thermodynamics of $NaO^+(X^3\Sigma^-)$: Relevance to Atmospheric Chemistry

Pavel Soldán,[†,‡,§] Edmond P. F. Lee,[†,||,⊥] and Timothy G. Wright*[†,∇]

Department of Chemistry, University of Southampton, Highfield, Southampton, U.K. SO17 1BJ,
J. Heyrovský Institute of Physical Chemistry, Academy of Science of the Czech Republic,
182 23 Prague 8, Dolejškova 3, Czech Republic, and Department of Applied Biology and
Chemical Technology, Hong Kong Polytechnic University, Hung Hom, Hong Kong

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The spectroscopy and thermodynamics of the atmospherically important $NaO^+(X^3\Sigma^-)$ species are calculated using high-level ab initio calculations, up to the RCCSD(T)/aug-cc-pV5Z level. The calculated dissociation energy was $D_0 = 0.29 \pm 0.02$ eV, which is to the low end of the range of values obtained from previous experimental studies. This lower value for the dissociation energy of NaO^+ has implications for experimental values of the dissociation energy of NaO and the adiabatic ionization energy (AIE) of NaO. Further calculations led to the dissociation energy of $NaO(X^2\Pi)$ being calculated as $D_0 = 2.71 \pm 0.07$ eV, with the AIE for the $NaO^+(X^3\Sigma^-) \leftarrow NaO(X^2\Pi)$ ionization being calculated as 7.55 ± 0.08 eV. The dissociation energy of NaO is to the high end of previous experimental determinations but agrees very well with previous ab initio calculations. The AIE is somewhat higher than the onset measured in a recent photoelectron experiment, and this is discussed. In addition, a potential energy curve and dipole moment function for $NaO^+(X^3\Sigma^-)$ are calculated at the RCCSD(T)/aug-cc-pVQZ level. From the potential energy curve, vibrational separations and rotational energy levels were calculated, and from the calculated rovibrational levels, thermodynamic quantities were derived. The low-energy region of the $NaO(X^2\Pi)$ potential energy curve is also calculated, allowing the lowest energy levels to be obtained. From the vibrational wave functions of the neutral and cationic states, Franck−Condon factors were calculated for the first photoelectron band, which corresponds to the $NaO^+(X^3\Sigma^-) \leftarrow NaO(X^2\Pi)$ ionization. The role of NaO^+ in atmospheric chemistry is discussed as well as the implications the present results have on a recently suggested model for the formation of sporadic sodium layers. It is noted that the $a^1\Delta$ state of NaO^+ will be metastable and so may have a role in atmospheric chemistry.

I. Introduction

The alkali-metal oxide molecules are of great importance in atmospheric chemistry,[1] energy technology,[2] flame chemistry,[3] and chemical lasers.[4] The cations of these species have, however, not been considered to a large extent, despite the fact that, owing to their low ionization energies, the cations will certainly be present in flames, plasmas, and the atmosphere. Indeed, Brown[5] summarized the information known about the (calculated) distribution in the Earth's atmosphere of NaO^+ ions in 1973: this indicated that there was a peak in the distribution of NaO^+ at ca. 90 km, followed by a dip at ca. 75 km, with a rising abundance to lower heights. This distribution was different from the NaO and NaO_2 distributions, suggesting that the cations did not arise simply via photoionization; the dip at ca. 75 km is close to a similar dip in the Na^+ distribution, suggesting that perhaps these two ionic species are linked. Very recently, Cox and Plane[6] have implicated NaO^+ in the formation of sporadic sodium layers. This latter inference is part of a wider suggestion that $Na^+{\cdot}X$ molecular complexes are responsible, at least in part, for the formation of these sporadic sodium layers.[7−9] This suggestion has arisen since, although there seems to be a correlation with the formation of sporadic sodium layers and sporadic electron layers, the rate of radiative recombination is too slow for it to link the two phenomena directly.[6,9] The model involves the formation of Na^+ via charge transfer from NO^+ and $O_2{}^+$ and its subsequent clustering to form $Na^+{\cdot}N_2$. The rate of production of neutral Na from dissociative neutralization with an electron is too high if this is the only cluster involved. It has been hypothesized that an O atom reacts with the $Na^+{\cdot}N_2$ complex and leads to NaO^+, which further reacts with an O atom to form $Na^+ + O_2$.[6] $Na^+{\cdot}N_2$ can ligand switch with CO_2, which can then also undergo dissociative neutralization with an electron. It is the destruction of $Na^+{\cdot}N_2$ by O, leading to NaO^+, that brings the calculated rate of neutral Na production in line with observations. The experiments in ref 6 showed that O could ligand switch with $Na^+{\cdot}N_2$ but not with $Na^+{\cdot}CO_2$, which was taken to infer that $D_0(Na^+{\cdot}N_2) \leq D_0(NaO^+) \leq D_0(Na^+{\cdot}CO_2)$, giving $0.35\ \text{eV} \leq D_0(NaO^+) \leq 0.69$ eV, where the values for the dissociation energies of the complexes were taken from ref 10.

NaO^+ has also been invoked to explain the luminosity of enduring meteor trails,[11] some of which can exist for some considerable time.[12]

Information on the NaO^+ ion is rather sparse. The dissociation energy has been deduced as 1.25 ± 0.7 eV from mass spectrometric experiments[13] and 0.8 ± 0.3 eV from merging beam studies,[14] each consistent (within the quoted experimental errors) with the most recent value deduced from photoelectron

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[†] University of Southampton.
[‡] Visiting Royal Society Fellow. E-mail: soldan@jh-inst.cas.cz.
[§] Academy of Science of the Czech Republic.
[||] Hong Kong Polytechnic University.
[⊥] E-mail: epl@soton.ac.uk.
[∇] E-mail: tgw@soton.ac.uk.

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studies by Wright et al.[15] of 0.60 ± 0.31 eV. The latter value was deduced using a D_0 value for the neutral of 2.56 ± 0.21 eV (ref 13) and the measured adiabatic ionization energy (AIE) of NaO(X$^2\Pi$) of 7.1 ± 0.1 eV (which was the onset of the first photoelectron band), but there are larger estimates for D_0[NaO(X$^2\Pi$)] from experimental studies of 2.91 ± 0.13 eV[16] and theoretical studies, 2.88 eV (CISD level).[17] Taking an encompassing value of 2.9 ± 0.2 eV for these would yield a value for D_0[NaO$^+$(X$^3\Sigma^-$)] of 0.9 ± 0.3 eV. On the other hand, Lee et al.[18] calculate D_0[NaO(X$^2\Pi$)] to be 2.43 eV, at the CISD level of theory, including the Davidson correction for quadruple excitations, which would yield D_0[NaO$^+$(X$^3\Sigma^-$)] = 0.5 ± 0.1 eV, where the possible error in the theoretical studies has been disregarded, and it has been assumed that the AIE from ref 15 is correct. (It is possible that the AIE of ref 15 is an underestimate, since the NaO produced in that work may have been internally excited.) Thus, the dissociation energies of both the ground-state neutral and cation are not yet well established, owing to the large errors and disparity of the experimental values.

It was the initial aim of the present work to employ high-level ab initio calculations in the calculation of the dissociation energy of NaO$^+$(X$^3\Sigma^-$) and also to calculate an accurate potential energy curve, from which rovibronic energy levels can be calculated. (The ground electronic state of NaO$^+$ has been shown to be $^3\Sigma^-$ by Wright et al. as part of their photoelectron and ab initio study of the alkali-metal oxides.[15]) From the calculated rovibrational energies, simple statistical mechanics may then be employed to calculate the enthalpy, entropy, and free energy of reaction for the process

$$\mathrm{NaO^+(X^3\Sigma^-)} \rightarrow \mathrm{Na^+(^1S)} + \mathrm{O(^3P)} \qquad (1)$$

and, consequently, the equilibrium constant. As it turns out, the calculated value for D_e[NaO$^+$(X$^3\Sigma^-$)] has consequences for the dissociation energy of NaO(X$^2\Pi$) and the AIE. Consequently, further calculations were performed to calculate D_e[NaO(X$^2\Pi$)] and the AIE [NaO$^+$(X$^3\Sigma^-$) ← NaO(X$^2\Pi$)].

II. Theoretical Methods

(a) NaO$^+$(X$^3\Sigma^-$). *(i) Dissociation Energies, D_e. SERHF and CISD Calculations*. A number of theoretical methods were employed to calculate the dissociation energy of NaO$^+$. First, it is important to note that when NaO$^+$(X$^3\Sigma^-$) is at its equilibrium bond length, it is essentially Na$^+$O and that at long bond lengths it is Na$^+\cdots$O, in *cylindrical* symmetry, whereas at an infinite separation, the atoms are *spherical* entities. Consequently, it is necessary to consider these points for the calculation of the dissociation energy.

The first set of calculations, using GAMESS-UK,[19] used the CISD method employing symmetry-equivalent restricted Hartree−Fock (SERHF) wave functions. (Note that in the SERHF and CISD calculations, the correct wave function is used in all cases, with the spherical O wave function being truly ^{3}P in character.) These were performed as follows: first, the geometry was optimized at the CISD level, and the total energy at the equilibrium geometry calculated using the SERHF and CISD approaches; second, the energy of the Na$^+\cdots$O ($^3\Sigma^-$) system at 100 Å was calculated for each method to give the energy of the system at (effectively) infinite separation in cylindrical symmetry (the supermolecule approach); third, a full counterpoise correction (CP) is performed *in cylindrical symmetry* at the equilibrium geometry to correct for basis set superposition error (BSSE); finally, the energy of O is calculated in spherical symmetry (^{3}P). Consequently, there are three distinct dissociation energies:

$$D_e(1) = E_e(\mathrm{NaO^+})_{100\,\text{Å}} - E_e(\mathrm{NaO^+})_{\mathrm{eqm}}$$

$$D_e(2) = D_e(1) + \mathrm{BSSE_{tot}}$$

$$\mathrm{BSSE_{tot}} = \mathrm{BSSE(Na^+)} + \mathrm{BSSE(O)}$$

$$\mathrm{BSSE(O)} = E_e[\mathrm{O(^3\Sigma^-)}] - E_e[\mathrm{O(^3\Sigma^-)(Na)_G}]_{\mathrm{eqm}}$$

where "eqm" implies the equilibrium separation, O($^3\Sigma^-$) implies a calculation performed on O in cylindrical symmetry, and $(\ )_\mathrm{G}$ implies a ghost center

$$D_e(3) = D_e(2) + \Delta E_e[\mathrm{O(^3P)} - \mathrm{O(^3\Sigma^-)}]$$

where O(^{3}P) implies that spherical symmetry is used.

Calculations at the CISD level were performed, both with (+Q) and without the Davidson correction for quadruple excitations. For the CISD calculations, the use of the supermolecule approach [the procedure for calculating D_e(1)] and the use of the Davidson correction help to correct for the lack of size consistency within this level of theory. In summary, therefore, D_e(1) is the dissociation energy obtained using the supermolecule approach, D_e(2) is D_e(1) but corrected for BSSE, and D_e(3) is D_e(2) corrected to the "real" spherically symmetric dissociation products.

Two basis sets were used in these calculations:

Basis 1 is the TZV basis set from ref 20, augmented with a set of diffuse s and p functions Na [exponents 0.008 (s) and 0.00543 (p)] and O [exponent 0.0845 (s and p)] and a set of three d and two f polarization functions Na [exponents 2.88, 0.72, and 0.18 (d); 1.2 and 0.35 (f)] and O [exponents 3.0, 1.0, and 0.3333 (d); 2.0 and 0.67 (f)].

Basis 2 is where the standard aug-cc-pVQZ basis set was used for O; for Na, the basis set is identical to a aug-cc-pVQZ basis set for neutral Na but has been optimized for Na$^+$; it has been described in detail in ref 21. Basically it is derived from the Na 27s20p basis set of Huzinaga, with the six most diffuse s and p functions discarded. In the derivation of this basis set, a Hartree−Fock calculation was performed on Na$^+$; from this, the 18 tightest expansion coefficients for the 1s orbital were kept as 1 contraction, all the 21 expansion coefficients were kept for the 2s orbital, and all the 14 expansion coefficients were kept for the 2p orbital. These three contracted basis functions were augmented with five uncontracted sp functions (exponents 4.5, 1.9565, 0.8507, 0.3699, and 0.1608), four d functions (exponents 1.85, 0.6852, 0.2538, and 0.093 99), and three f functions (exponents 1.2, 0.4, and 0.1333). Note that the augmentation functions used here for Na$^+$ are slightly more tight than those used in ref 21; this was because a linear dependence in those basis functions was found, probably owing to the use of Cartesian d and f functions, as necessitated by the use of the GAMESS-UK program here. (For all other calculations reported here, spherical harmonics were employed.)

UMP2, UQCISD, and UQCISD(T) Calculations. It was then decided to attempt other calculations, where the O wave function is symmetry broken, but the methods are size consistent. The levels attempted were UMP2, UQCISD, and UQCISD(T) using the aug-cc-pVTZ basis set, where again the sodium basis set was derived for Na$^+$ and is exactly as described in ref 21. Although there is a potential problem with spin contamination here, since unrestricted wave functions are being used, in all

TABLE 1: Calculated Dissociation Energies (eV) of NaO$^+$(X$^3\Sigma^-$) Using Basis Sets 1 and 2 and the SERHF and CISD(+Q) Levels of Theory[a]

	SERHF	CISD[b]	CISD+Q[b]
basis 1			
$D_e(1)$	0.267	0.294	0.300
$D_e(2)$	0.266	0.287	0.293
$D_e(3)$	0.346	0.298	0.288
basis 2			
$D_e(1)$	0.268	0.299	0.305
$D_e(2)$	0.267	0.290	0.296
$D_e(3)$	0.349	0.301	0.291

[a] See text for details. For the CISD(+Q) calculations, all electrons are included in the correlation treatment. The bond length used is 2.535 Å, which is the optimized value at the CISD level (using either basis set). [b] CISD leading coefficients ~0.97 for basis 1 and 0.98 for basis 2.

TABLE 2: Calculated Dissociation Energies (eV) of NaO$^+$(X$^3\Sigma^-$) at the Unrestricted MP2, QCISD, and QCISD(T) and Restricted CCSD(T) Levels of Theory[a]

	UMP2	UQCISD	UQCISD(T)[b]	RCCSD(T)	
basis set	aug-cc-pVTZ	aug-cc-pVTZ	aug-cc-pVTZ	aug-cc-pVQZ	aug-cc-pV5Z[c]
D_e	0.305	0.305	0.308	0.315	0.315
D_e + BSSE	0.291	0.292	0.295	0.299	0.301

[a] See text for details. For these calculations, the frozen core approximation was used, with the following orbitals frozen: for the UMP2, Na 1s and 2s and O 1s; for UQCISD/UQCISD(T), Na 1s and O 1s; for RCCSD(T), Na 1s. For the UMP2 and UQCISD calculations, the optimized bond length was 2.496 Å; for the RCCSD(T) calculations, the value was 2.493 Å. [b] Single-point calculations at the UQCISD-optimized geometry. [c] Single-point calculations at the RCCSD(T)/aug-cc-pVQZ equilibrium geometry.

cases the spin contamination was small, with $\langle S^2 \rangle$ values < 2.1. (A value of 2 is expected for a pure triplet state.) All calculations reported in this subsection were performed with Gaussian94.[22]

RCCSD(T) Calculations. Finally, a set of RCCSD(T) calculations was undertaken. For these calculations, the aug-cc-pVQZ basis set for Na was used, as optimized for Na$^+$, and is exactly as described in ref 21. Rather than optimizing the geometry using analytic gradient techniques, a point-by-point counterpoise-corrected potential energy curve was calculated using bond lengths from 1.7 to 150 Å. Finally, RCCSD(T)/aug-cc-pV5Z//RCCSD(T)/aug-cc-pVQZ calculations were performed, where the basis set for sodium was that optimized for Na$^+$, from ref 21, but augmented with two h functions (exponents 0.5 and 0.12). The RCCSD(T) calculations, in this and the following, were performed using MOLPRO.[23]

(b) Calculations on NaO(X$^2\Pi$). NaO(X$^2\Pi$) is an ionic molecule at its equilibrium bond length but dissociates to yield neutral products. Consequently, there is an avoided crossing between two $^2\Pi$ states between the equilibrium geometry and the dissociation limit, as calculated in ref 24. For the purposes of these calculations, this was not important, as calculations are only performed at the equilibrium geometry and at infinite separation. (For the calculation of high-lying rovibrational levels, however, this avoided crossing will have a dramatic effect on the calculated energies.) As with NaO$^+$, the equilibrium geometry was extracted from a CP-corrected potential energy curve calculated in a point-by-point fashion at the RCCSD(T)/aug-cc-pVQZ level of theory. In addition, the zero-point level and 1−0 separation were calculated. In the single-point calculations, it was checked that at the longest bond lengths used (4 Å), the wave function was adequately described by a single reference by calculating the T1 diagnostic: at 4 Å, the value was 0.015, which is less than 0.021, the critical value for indicating the onset of multireference behavior,[25] so the calculated potential curve for NaO(X$^2\Pi$) ought to be reliable. Finally, RCCSD(T) calculations were performed in a similar way to those for NaO$^+$(X$^3\Sigma^-$).

III. Results

(a) Bond Length and Dissociation Energy of NaO$^+$(X$^3\Sigma^-$). *SERHF and CISD.* The calculated dissociation energies, D_e, using the two basis sets and the SERHF and CISD (+Q) approaches are given in Table 1. The bond length, r_e, used is 2.535 Å, which was the optimized value at the CISD level and was the same for both basis sets. As may be seen, both basis sets are suggesting a value of 0.3 eV for D_e[NaO$^+$(X$^3\Sigma^-$)]. The inclusion of quadruple excitations via the Davidson correction appears not to be totally reliable here, since after correction from cylindrical to spherical symmetry it is expected that the dissociation energy will rise; however, a decrease occurs for the CISD+Q calculations [compare $D_e(2)$ to $D_e(3)$]. We conclude that the Davidson correction is not a sufficiently good approximation here, and the small difference in the leading coefficients in the CI expansion between the cylindrical and spherical O wave functions is leading to the unexpected behavior.

UMP2, UQCISD, UQCISD(T), and RCCSD(T). The bond length was optimized at the UMP2 and UQCISD levels: both yielded values of 2.496 Å. The dissociation energy was then calculated and corrected for BSSE, with the UQCISD(T) calculations being performed at the UQCISD-optimized geometry. The values obtained are given in Table 2.

As noted above, a potential energy curve was calculated at the RCCSD(T) level. From this curve, the equilibrium bond length was calculated as 2.493 Å and is expected to be quite accurate. In addition, the D_e value (inherently corrected for BSSE) was derived as 0.299 eV (Table 2). The potential energy curve will be considered in more detail in the following subsection.

(b) Potential Energy Curve and Vibrational and Rovibrational Energy Levels of NaO$^+$(X$^3\Sigma^-$). As noted above, a set of total energies was calculated at the RCCSD(T)/aug-cc-pVQZ level. The energy and calculated dipole moment function values are given in Table 3. From the potential energy curve, the vibrational and rovibrational energy levels were calculated using LeRoy's LEVEL program;[26] from these values, the zero-point energy value could be evaluated explicitly, allowing D_0 to be calculated as 0.2875 eV, where anharmonicity is implicitly accounted for. The lowest vibrational levels are given in Table 4. Overall, 2524 bound rovibrational states were calculated, and these were used in the calculation of thermodynamic quantities below. The value of the 1−0 separation (181 cm^{-1}) may be compared to the previously calculated value for ω_e of 207.4 cm^{-1} at the CISD+Q level of theory (no account for BSSE);[15] in addition, the calculated bond length, r_e = 2.528 Å of ref 15, also compares favorably with the values calculated here (vide supra).

As may be seen from the lowest few values in Table 4, the anharmonicity in this species is substantial, with the lowest vibrational separations calculated to be 181.8, 172.4, 163.1, 153.9, 144.9, and 136.0 cm^{-1}. Consequently, it may be expected that use of the harmonic oscillator approximation to calculate thermodynamic quantities would not lead to reliable values. Since, from LEVEL, all the bound rovibrational levels

TABLE 3: Total Energy (cm^{-1}) and Dipole Moments (D) of $NaO^+(X^3\Sigma^-)$ as a Function of Bond Length (Å)[a]

r	$V(r)$	$D(r)$	r	$V(r)$	$D(r)$
1.70	12855.886 756	−2.999 598	3.30	−1374.319 416	−6.133 878
1.80	6893.033 167	−3.129 698	3.35	−1311.422 376	−6.242 909
1.90	3075.195 136	−3.275 845	3.40	−1251.334 611	−6.351 687
2.00	669.145 230	−3.436 191	3.45	−1194.082 459	−6.460 196
2.10	−808.300 926	−3.609 044	3.50	−1139.613 245	−6.568 614
2.15	−1303.310 594	−3.699 647	3.75	−906.054 926	−7.104 739
2.20	−1676.527 204	−3.792 763	4.00	−727.799 825	−7.634 457
2.25	−1951.476 244	−3.888 190	4.25	−591.712 385	−8.158 418
2.30	−2147.333 210	−3.985 728	4.50	−486.759 617	−8.675 776
2.35	−2279.759 813	−4.085 182	4.75	−404.777 063	−9.189 898
2.40	−2361.527 282	−4.186 358	5.00	−339.917 920	−9.700 697
2.45	−2403.065 051	−4.289 072	5.50	−246.204 447	−10.714 612
2.50	−2412.888 735	−4.393 144	6.00	−184.295 043	−11.721 089
2.55	−2397.927 150	−4.498 493	6.50	−141.870 597	−12.722 419
2.60	−2363.838 350	−4.604 782	7.00	−111.675 277	−13.720 133
2.65	−2315.218 135	−4.711 946	7.50	−89.525 897	−14.715 320
2.70	−2255.786 599	−4.819 840	8.00	−72.834 851	−15.708 223
2.75	−2188.541 767	−4.928 349	9.00	−50.121 422	−17.690 900
2.80	−2115.950 533	−5.037 323	10.00	−35.943 360	−19.670 130
2.85	−2039.944 273	−5.146 666	12.50	−17.863 040	−24.610 448
2.90	−1962.070 284	−5.256 274	15.00	−10.128 754	−29.543 757
2.95	−1883.564 209	−5.366 060	20.00	−4.163 434	−39.404 648
3.00	−1805.387 345	−5.475 942	30.00	−1.196 137	−59.116 351
3.05	−1728.281 517	−5.585 849	50.00	−0.245 812	−98.532 968
3.10	−1652.821 750	−5.695 720	75.00	−0.065 842	−147.801 296
3.15	−1579.431 628	−5.805 500	100.00	−0.021 947	−197.068 997
3.20	−1508.416 221	−5.915 145	125.00	−0.006 584	−246.336 341
3.25	−1440.014 757	−6.024 616	150.00	0.000 000	−295.603 899

[a] Energy is given relative to the dissociation products.

TABLE 4: Rotational Constants of $NaO^+(X^3\Sigma^-)$ for the Lowest Vibrational Energy Levels (cm^{-1})[a]

v	$E(v,0)$	J^*	B_v	$\times 10^6 D_v$	$\times 10^{11} H_v$
0	0	16	0.2835	2.647	−2.946
1	181.76	16	0.2752	2.743	−3.381
2	354.12	16	0.2668	2.849	−3.883
3	517.21	15	0.2583	2.963	−4.449
4	671.15	15	0.2498	3.088	−5.124
5	816.06	14	0.2411	3.222	−5.898

[a] $E(v,J) = E(v,0) + B_vJ(J+1) - D_vJ^2(J+1)^2 + H_vJ^3(J+1)^3$. Although it was possible to fit higher order centrifugal distortion coefficients, the three quoted rotational constants reproduce the "exact" rotational energy levels to within 1×10^{-5} cm^{-1}, up to the J^* value given in the third column.

are available, then it is relatively straightforward to evaluate partition functions explicitly and, consequently, enthalpies, entropies, and free energies (vide infra).

It was also possible to calculate the rotational energy levels of $NaO^+(X^3\Sigma^-)$ for all of the vibrational levels up to dissociation; however, only the results for $v = 0-5$ are given here (Table 4). These are provided to help guide a possible microwave experiment, although such an experiment would see more than just the pure rotational structure, as spin−rotation and hyperfine interactions will also be present. The dipole moment, with respect to the center of mass, at the equilibrium bond length is 4.378 D, or 4.428 D at the r_0 separation ($r_0 = 2.517$ Å, calculated using LEVEL).

(c) Thermodynamic Quantities for $NaO^+(X^3\Sigma^-)$. Since we have calculated the rovibrational levels explicitly, then it is possible to calculate the enthalpy and entropy for the $NaO^+ \rightarrow Na^+ + O$ process explicitly, using simple statistical mechanics in the canonical ensemble but without having to resort to the use of the rigid-rotor, simple harmonic oscillator (RRHO) approximation. This was done using simple computer programs written in-house. At 298 K and 1 atm, the calculated values are $\Delta S = 62.2$ J K^{-1} mol^{-1}, $\Delta H = 29.6$ kJ mol^{-1}, and $\Delta G = +11.04$ kJ mol^{-1}, which gives an equilibrium constant of 0.012. It is of interest to see how the equilibrium constant for formation of NaO^+ varies as a function of pressure and temperature (assuming there will always be a third body available). To do this, ΔS and ΔH were calculated at the typical temperatures and pressures at various heights above ground level, taken from ref 27, and these, together with the derived ΔG and equilibrium constant, are given in Table 5. From these data, it is possible to calculate the concentrations (or ratios of concentrations), given the partial pressures or number densities of Na^+, O, or NaO^+ in the atmosphere; however, since NaO^+ may arise from a number of different routes and since equilibrium may not be established at all points, we refrain from doing so here. The data should prove useful as input to more complicated reaction modeling schemes.

(d) $NaO(X^2\Pi)$. From the potential energy curve calculated for $NaO(X^2\Pi)$ at the RCCSD(T) level, the 1−0 separation was calculated as 485.1 cm^{-1}, which may be compared to the experimental value[28] of $\omega_e = 492.27$ cm^{-1} [estimated from the experimental values for the rotational constant, B_e, and the centrifugal distortion coefficient, D_e, from the expression $\omega_e = \{(4B_e^3)/D_e\}^{1/2}$]. For comparison, the r_e value was calculated as 2.056 Å, which compares with the experimental value of 2.0515 Å (the r_0 value was evaluated as 2.064 Å).

The dissociation energy was obtained as for $NaO^+(X^3\Sigma^-)$, at the RCCSD(T)/aug-cc-pVQZ basis set, and yielded a value of $D_e = 2.94$ eV ($D_0 = 2.91$ eV); using an aug-cc-pV5Z basis set, the calculated D_e was 2.74 eV.

IV. Discussion

(a) Dissociation Energy of $NaO^+(X^3\Sigma^-)$. As may be seen from Tables 1 and 2, the dissociation energy of $NaO^+(X^3\Sigma^-)$ has been calculated to be ∼0.3 eV at all correlated levels of theory. At the highest levels of theory, a value of 0.30 was obtained; subsequently, we performed RCCSD(T) calculations with aug-cc-pV5Z basis sets at the RCCSD(T)/aug-cc-pVQZ

TABLE 5: Calculated Thermodynamic Quantities for the $NaO^+ \rightarrow Na^+ + O$ Reaction at Various Altitudes (the Requisite Third Body Is Assumed To Be Present at All Times)[a]

h	T	p	ΔS	ΔH	ΔG	ΔK
0	300.00	101325	62.18	29 567.07	10912.71	0.013
0	288.00	101325	62.12	29 550.31	11658.56	0.008
5	256.00	54050	67.12	29 487.70	12305.54	0.003
10	223.00	26500	72.66	29 396.52	13193.00	0.001
15	217.00	12110	79.08	29 377.13	12215.78	0.001
20	217.00	5529	85.60	29 377.13	10801.21	0.003
25	222.00	2549	92.12	29 393.35	8943.77	0.008
30	227.00	1197	98.47	29 408.97	7056.37	0.024
35	237.00	574.6	104.70	29 438.42	4624.85	0.096
40	250.00	287.1	110.61	29 473.09	1820.57	0.417
45	264.00	149.1	116.19	29 505.78	−1167.10	1.702
50	271.00	79.78	121.44	29 520.28	−3389.64	4.501
55	261.00	42.53	126.59	29 499.19	−3540.76	5.112
60	247.00	21.96	131.95	29 465.46	−3126.86	4.584
65	233.00	10.93	137.59	29 426.93	−2632.27	3.891
70	220.00	5.221	143.56	29 386.93	−2196.13	3.322
75	208.00	2.388	149.87	29 346.46	−1827.33	2.877
80	198.00	1.052	156.51	29 310.12	−1679.03	2.773
85	189.00	0.4457	163.47	29 275.36	−1620.78	2.805
86	187.00	0.3734	164.90	29 267.37	−1569.08	2.743
90	187.00	0.1836	170.80	29 267.37	−2672.82	5.579
95	189.00	0.07597	178.18	29 275.36	−4401.15	16.456
100	195.00	0.03201	185.49	29 298.75	−6871.91	69.300
110	240.00	0.007104	198.69	29 446.79	−18239.79	9325.808

[a] h is the altitude (km), T is the temperature (K), p is the pressure (Pa), ΔS is the entropy change (J K^{-1} mol^{-1}), ΔH is the enthalpy change (J mol^{-1}), ΔG is the Gibbs free-energy change (J mol^{-1}), and K is the equilibrium constant obtained using the equation $\Delta G = -RT \ln K$.

equilibrium geometry, which also led to a value of 0.30 eV. Consequently, our best estimate of D_e for $NaO^+(X^3\Sigma^-)$ at this level of theory is 0.30 ± 0.02 eV. The D_0 value, calculated with the zero-point energy from the RCCSD(T)/aug-cc-pVQZ potential energy curve, is 0.29 ± 0.02 eV [where the quoted error arises from the size of the BSSE (0.02 eV)]. This value is significantly below the mass spectrometric values[13] of 1.25 ± 0.7 and 0.8 ± 0.3 eV from the merging beams study[14] and is only just within the lower bound of the value of 0.60 ± 0.31 eV derived from the photoelectron spectrum.[15] There are two possible reasons for this: (i) the dissociation energy of NaO used in ref 15 is too low, or (ii) the measured AIE is too low. In ref 15, NaO was produced by the reaction of Na with N_2O, and this was thought to produce NaO predominantly in the $A^2\Sigma^+$ state: the $X^2\Pi$ state was thought to be produced by collisional deactivation. It is thus possible for the onset of the photoelectron band in ref 15 to be lower than the AIE, e.g., if significant vibrational excitation of the ground state is present. (Note that $NaO^+(X^3\Sigma^-)$ cannot be accessed from $NaO(A^2\Sigma^+)$ in a one-electron process.) Using the value of $D_0[NaO^+(X^3\Sigma^-)] = 0.29 \pm 0.02$ eV obtained herein would yield a value for the AIE of 7.4 ± 0.2 eV, assuming that the value of $D_0[NaO(X^2\Pi)] = 2.56 \pm 0.21$ eV (ref 13) is correct and using IE(Na) = 5.14 eV. However, performing similar calculations to those presented here on $NaO(X^2\Pi)$ suggests that $D_0[NaO(X^2\Pi)] = 2.71 \pm 0.07$ eV (see next subsection), a value that is just outside the error range of an experimental value from Herm and Herschbach,[16] 2.91 ± 0.13 eV, but in very good agreement with the value of 2.76 ± 0.04 eV from ref 29 vide infra.

(b) Dissociation Energy, Equilibrium Bond Length and Fundamental Vibrational Frequency of $NaO(X^2\Pi)$. The value of $D_e = 2.94$ eV ($D_0 = 2.91$ eV) calculated here at the RCCSD(T)/aug-cc-pVQZ level is somewhat higher than the value reported previously by us[18] but is close to the value of $D_e = 2.91$ eV reported by Langhoff et al.:[17] the lower value in ref 18 probably results from a basis set that is too small. Further, we calculated the dissociation energy employing a aug-cc-pV5Z basis set, as noted above, yielding a value of $D_e = 2.74$ eV, indicating that a large, flexible basis set is required to calculate this quantity. This is not so surprising (in retrospect), as the dissociation is taking a Na^+O^- molecule to Na + O products, so it is necessary that the basis sets are sufficient to describe Na and Na^+ and O and O^-. In ref 21, we have shown that using a basis set optimized for neutral Na leads to very poor behavior at the correlated level for Na^+. There are two ways of testing this: (i) the calculated BSSE for the $Na^+{\cdot}O^-$ system at the equilibrium geometry and (ii) the calculated ionization energy of Na and electron affinity of O. Test ii is a good test of the reliability of the calculations, since the dissociation process here largely involves a neutralization of Na^+ and an electron detachment from O. Using the aug-cc-pVQZ basis set from ref 21, the calculated ionization energy of Na was 4.90 eV, and the calculated electron affinity of O was 1.40 eV, suggesting that the calculated dissociation energy may have an error of ~0.3 eV when compared to the experimental values of 5.139 eV for IE(Na)[30] and 1.461 eV for EA(O).[31] The BSSE in this case was calculated to be 0.03 eV, so the overall dissociation energy may be quoted as $D_e = D_0 = 2.9 \pm 0.3$ eV at the RCCSD(T)/aug-cc-pVQZ level. To check the calculated dissociation energy of $NaO(X^2\Pi)$ further, RCCSD(T)/aug-cc-pV5Z calculations were used, where again the basis set used for sodium has been optimized for Na^+ and is described fully in ref 21. The calculated ionization energy of Na is 5.13 eV, and the calculated electron affinity of O is 1.43 eV using this method, implying that the error in the dissociation energy from these discrepancies should be ~0.04 eV. The RCCSD(T)/aug-cc-pV5Z calculation was performed at the RCCSD(T)/aug-cc-pVQZ optimized bond length and yielded the value of $D_e = 2.74 \pm 0.07$ eV mentioned above (where the quoted error arises from the discrepancies between the computed and experimental values of IE(Na) and AE(O) and the BSSE; this is expected to be the maximum error). This D_e value may then be corrected for zero-point energy, with the value taken from the RCCSD(T)/aug-cc-pVQZ calculations, giving $D_0 = 2.71 \pm 0.07$ eV. Having now obtained reliable values for the dissociation energies of $NaO(X^2\Pi)$ and $NaO^+(X^3\Sigma^-)$, it is possible to calculate the adiabatic ionization energy of $NaO(X^2\Pi)$, using the equation

$$\mathrm{AIE} = D_0(\mathrm{NaO}) - D_0(\mathrm{NaO}^+) + \mathrm{IE(Na)}$$

At the RCCSD(T)/aug-cc-pVQZ level of theory, this yielded a value of 7.52 eV, and at the RCCSD(T)/aug-cc-pV5Z level of theory, this yielded a value of 7.55 eV, which indicates that saturation of the basis set is almost complete for calculation of this quantity. (The correction from D_e to D_0 in both cases was performed by using the energy of the zero point from the RCCSD(T)/aug-cc-pVQZ potential energy surface, as obtained from the vibrational levels calculated using LEVEL.) Calculating the AIE from the difference in the zero-point levels also yields a value of 7.55 eV at the CCSD(T)/aug-cc-pV5Z level, as expected.

(c) Franck−Condon Factors. Since the vibrational wave functions for both $NaO(X^2\Pi)$ and $NaO(X^3\Sigma^-)$ have been calculated, it is possible to calculate the Franck−Condon factors (FCFs) directly from these. The results of these calculations are shown in Table 6. As may be seen, the photoelectron band corresponding to the $NaO^+(X^3\Sigma^-) \leftarrow NaO(X^2\Pi)$ ionization is expected to be ca. 0.3 eV broad, with an onset at 7.52 eV [CCSD(T)/aug-cc-pVQZ value] and a maximum (the vertical ionization energy, VIE) at ca. 7.7 eV. The VIE agrees very

TABLE 6: Franck−Condon Factors (FCFs), Normalized to the Most Intense Component, for the Ionization $NaO^+(X^3\Sigma^-, v') \leftarrow NaO(X^2\Pi, v'' = 0)$[a]

v'	J_{max}	$E(v',0)$	FCF
0	94	0.000 000	0.005 798
1	92	181.756 180	0.031 287
2	90	354.124 720	0.091 555
3	87	517.212 455	0.193 299
4	85	671.149 646	0.330 549
5	83	816.063 790	0.487 242
6	81	952.099 951	0.643 490
7	78	1079.415 946	0.781 594
8	76	1198.192 935	0.889 341
9	74	1308.620 691	0.960 995
10	72	1410.927 410	0.996 711
11	70	1505.366 378	1.000 000
12	68	1592.217 573	0.977 003
13	66	1671.799 862	0.934 195
14	64	1744.464 377	0.878 092
15	62	1810.591 663	0.813 927
16	60	1870.573 361	0.746 085
17	59	1924.807 037	0.677 637
18	57	1973.687 562	0.610 808
19	55	2017.596 374	0.546 926
20	53	2056.892 625	0.486 730
21	52	2091.913 272	0.430 628
22	50	2122.979 907	0.378 904
23	48	2150.414 032	0.331 840
24	47	2174.543 884	0.289 529
25	45	2195.693 649	0.251 819
26	44	2214.171 115	0.218 372
27	42	2230.260 168	0.188 810
28	40	2244.226 367	0.162 854
29	39	2256.308 925	0.139 925
30	38	2266.706 064	0.119 562
31	36	2275.605 033	0.101 780
32	35	2283.198 453	0.086 469
33	33	2289.652 970	0.073 054
34	32	2295.101 087	0.061 297
35	31	2299.665 290	0.051 018
36	29	2303.457 320	0.042 228
37	28	2306.598 474	0.034 851
38	27	2309.183 100	0.028 507
39	25	2311.289 716	0.023 049
40	24	2312.986 859	0.018 533
41	23	2314.347 028	0.014 764
42	21	2315.422 698	0.011 504
43	20	2316.250 846	0.008 818
44	19	2316.889 370	0.006 828
45	18	2317.391 135	0.005 460

[a] Only FCFs Greater than 0.005 have been included: in fact there are 54 bound vibrational states of NaO^+. $J_{max} + 1$ is the maximum number of bound rotational levels.

well with the first photoelectron band maximum in ref 15 [7.70 ± 0.06 eV], but the AIE is significantly higher than the photoelectron band onset of 7.1 ± 0.1 eV. There could be a number of reasons for the lower value measured in ref 15. For example, the NaO was produced from the reaction $Na + N_2O \rightarrow NaO + N_2$ for the spectrum that shows the onset most clearly. Consequently, the $NaO(X^2\Pi)$ that was produced could reasonably be expected to be vibrationally excited, as mentioned in ref 15; in addition, there may also be rotational broadening from thermal effects, as well as from the reaction. Another point to note is that it was hypothesized that NaO was also (predominantly) produced in the $A^2\Sigma^+$ state from the reaction and that the $X^2\Pi$ was produced by collisional deactivation. The $A^2\Sigma^+$-state cannot be the cause of the low onset, since it cannot access the $X^3\Sigma^-$ state of NaO^+ in a one-electron ionization. It is clear from the FCFs (Table 6) that the adiabatic ionization energy will be very weak and difficult to resolve in a conventional photoelectron experiment. To observe the photoelectron band clearly, it will be necessary to produce the NaO in a cold environment, such as a molecular beam, and to use a high-resolution form of photoelectron spectroscopy, such as zero-kinetic energy (ZEKE) spectroscopy.[32]

(d) Atmospheric Relevance. As noted in the Introduction, Cox and Plane[6] have put forward the idea that O atoms attack $Na{\cdot}N_2^+$ complexes, leading to a slowing down in the rate of production of neutral Na atoms via dissociative neutralization: $Na^+{\cdot}N_2 + e^- \rightarrow Na + N_2$. The attack occurs as a ligand switch, viz. $Na^+{\cdot}N_2 + O \rightarrow NaO^+ + N_2$. The NaO^+ is then itself destroyed by attack from O atoms, giving back Na^+ and also O_2. Whether the ligand switch of N_2 for O occurs or not depends on the heat of reaction for the switching process. Cox and Plane[6] showed that the ligand switch did occur in a low-temperature fast-flow reactor but that O did not ligand switch with CO_2 in $Na^+{\cdot}CO_2$ complexes, and they consequently deduced that $D_0(NaO^+)$ was bounded by the values 0.35 and 0.69 eV; in particular, $D_0(NaO^+) \geq 0.35$ eV. The latter result is in contradiction to our results here. We are confident that our value is correct, however, since the basis sets and theoretical methods used give values which converged, and in addition, we have tested the methodology by calculating such quantities as IE(Na) and EA(O) and obtain very good agreement with the known values. Since $D_0(NaO^+) \geq 0.35$ eV actually arises from $D_0(NaO^+) \geq D_0(Na^+{\cdot}N_2)$, we have also calculated the second quantity[33] at the CCSD(T)/aug-cc-pVQZ level and obtain a value of $D_0[Na^+{\cdot}N_2] \sim 0.31 \pm 0.02$ eV, indicating that the proposed ligand-switch reaction is thermodynamically (just) possible. It should be noted, however, that it is actually the free energy of the ligand-switching reaction that is important, and this will depend on the local pressure and temperature of the atmosphere. In the case of $NaO^+(X^3\Sigma^-)$, the variation was calculated (see above and Table 5), which should prove useful in modeling the $[NaO^+]$ distribution, from the known cation chemistry.

As well as its production from ligand switching with $Na^+{\cdot}N_2$, NaO^+ can presumably form via photoionization and charge-transfer reactions. The photoelectron experiments of ref 15 showed that there were six ionic states of NaO^+ lying within 3.6 eV. Five of these are accessible by photoionization of $NaO(X^2\Pi)$, with three accessible from $NaO(A^2\Sigma^+)$. Three of the NaO^+ electronic states arise from the configuration $\sigma^2\pi^2$, giving the $X^3\Sigma^-$, $a^1\Delta$, and $c^1\Sigma^+$ states, with the $A^3\Pi$ and $b^1\Pi$ states arising from a $\sigma^1\pi^3$ configuration. The stability of $NaO^+(X^3\Sigma^-)$ depends on the temperature and pressure, and Table 5 indicates that the equilibrium position of the $Na^+ + O \rightarrow NaO^+$ reaction depends a lot on altitude. Presumably some of the other cationic states may also be accessed in charge- and ligand-transfer reactions. The $a^1\Delta$ state should be metastable, as a transition to the ground state involves $\Delta S = 1$ and $\Delta\Lambda = 2$; the other states should be able to transfer to either the a or X states, in one step or two steps. Consequently, the chemistry of NaO^+ should take into account that there are these two states available for reaction. In a future piece of work, we will consider all these low-lying cationic states of sodium monoxide. It is, however, possible to estimate the dissociation energy of the $a^1\Delta$ state by noting that it dissociates to $Na^+(^1S) + O(^1D)$. From the known $O(^1D) \leftarrow O(^3P)$ separation (15 867.7 cm^{-1}),[30] and the difference between the calculated AIEs[15] for the ionizations $NaO^+(a^1\Delta) \leftarrow NaO(X^2\Pi)$ and $NaO^+(X^3\Sigma^-) \leftarrow NaO(X^2\Pi)$, 0.94 eV [although the absolute AIEs in ref 15 are too low, as compared to the result for NaO^+ $(X^3\Sigma^-)$ in the present paper, since the same electron is removed in the ionization, and since the same $\sigma^2\pi^2$ configuration results, the difference in the AIEs is expected to be reasonably accurate], and the calculated dissociation energy of $NaO^+(X^3\Sigma^-)$ calculated herein, $D_0[NaO^+(a^1\Delta)] \sim 1.31$ eV, indicating that it should be more stable than its ground-state counterpart.

V. Conclusions

We have used high-level ab initio calculations to calculate the dissociation energy of $NaO^+(X^3\Sigma^-)$ and obtain a value of $D_0 = 0.29 \pm 0.02$ eV. In addition, we calculated the dissociation energy of $NaO(X^2\Pi)$, obtaining a value of 2.71 ± 0.07 eV at the highest level of calculation used. These values gave a value for AIE[$NaO(X^2\Pi)$] of 7.55 ± 0.08 eV. These values were compared to the available experimental values, where possible.

We have also presented a potential energy curve and the dipole moment function for $NaO^+(X^3\Sigma^-)$, from which anharmonic vibrational frequencies and rotational energy levels are calculated. From the rovibrational energy levels obtained, thermodynamic quantities were calculated using simple statistical mechanics. The results indicate that NaO^+ could very well be involved in ligand-switching reactions, which have been hypothesized to lead to the formation of sporadic sodium layers by Cox and Plane. We also conclude that the $a^1\Delta$ state of NaO^+ may be present in the atmosphere and in other experiments where NaO is ionized.

Note Added in Proof. Recently, we have calculated the heat of formation of $NaO^+(X^3\Sigma^-)$ and $NaO(X^2\Pi)^{34}$ using the same basis sets and methods as here.

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References and Notes

(1) Wayne, R. P. *Chemistry of Atmospheres*, 2nd ed.; OUP: Oxford, 1991.

(2) Gole, J. L. *Opt. Eng.* **1981**, *20*, 5465.

(3) Hynes, A. J.; Steinberg, M.; Schofield, K. *J. Chem. Phys.* **1984**, *80*, 2585. Jensen, D. *J. Chem. Soc., Faraday Trans. 1* **1982**, *78*, 2835. Newman, R. N.; Payne, J. F. B. *Combust. Flame* **1978**, *33*, 291.

(4) Benard, D. J.; Benson, R. C.; Walker, R. E. *Appl. Phys. Lett.* **1973**, *35*, 161. Benson, R. C.; Bergeron, C. B.; Walker, R. E. *Chem. Phys. Lett.* **1975**, *35*, 161. Bernard, D. *J. Chem. Phys. Lett.* **1975**, *35*, 167.

(5) Brown, T. L. *Chem. Rev.* **1973**, *73*, 645.

(6) Cox, R. M.; Plane, J. M. C. *J. Geophys. Res.-Atmos.* **1998**, *D103*, 6349.

(7) Richter, E. S.; Sechrist, C. F., Jr. *J. Atm. Terr. Phys.* **1979**, *41*, 579.

(8) Plane, J. M. C. *Int. Rev. Phys. Chem.* **1991**, *10*, 55.

(9) Cox, R. M.; Plane, J. M. C. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 2619.

(10) Castleman, A. W., Jr.; Keesee, R. G. *Chem. Rev.* **1986**, *86*, 589.

(11) Poole, L. M. G. *J. Atm. Terr. Phys.* **1979**, *41*, 53.

(12) Baggaley, W. J. *Nature* **1981**, *289*, 530.

(13) Hildenbrand, D. L.; Murad, E. *J. Chem. Phys.* **1970**, *53*, 3403. Hildenbrand, D. L. Personal communication.

(14) Rol, P. K.; Entemann, E. A. *J. Chem. Phys.* **1968**, *49*, 1430.

(15) Wright, T. G.; Ellis, A. M.; Dyke, J. M. *J. Chem. Phys.* **1993**, *98*, 2891.

(16) Herm, R. R.; Herschbach, D. R. *J. Chem. Phys.* **1970**, *52*, 5783.

(17) Langhoff, S. R.; Bauschlicher, C. W.; Partridge, H. *J. Chem. Phys.* **1986**, *84*, 4474.

(18) Lee, E. P. F.; Wright, T. G.; Dyke, J. M. *Mol. Phys.* **1992**, *77*, 501; **1994**, *82*, 1281.

(19) GAMESS-UK: Guest, M. F.; Kendrick, J. *GAMESS User Manual*, CCP1/81/1; SERC Daresbury Laboratory, Warrington, U.K.

(20) Dunning, T. H., Jr. *J. Chem. Phys.* **1971**, *55*, 716. McLean, A. D.; Chandler, G. S. *J. Chem. Phys.* **1980**, *72*, 5639.

(21) Soldán, P.; Lee, E. P. F.; Wright, T. G. *J. Chem. Soc., Faraday Trans.*, in press. Note that in this reference, the derived aug-cc-pVXZ basis sets for Na^+ are denoted C-Huz-X.

(22) *Gaussian 94* (Revision E.1), M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheesemans, T. W. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, and J. A. Pople, Gaussian Inc., Pittsburgh, PA, 1995.

(23) MOLPRO is a package of ab initio programs written by H.-J. Werner, P. J. Knowles, with contributions from J. Almlöf, R. D. Amos, A. Berning, M. J. O. Deegan, F. Eckert, S. T. Elbert, C. Hampel, R. Lindh, W. Meyer, A. Nicklass, K. Peterson, R. Pitzer, A. J. Stone, P. R. Taylor, M. E. Mura, P. Pulay, M. Schuetz, H. Stoll, T. Thorsteinsson, and D. L. Cooper. With the CCSD treatment being described in: Hampel, C.; Peterson, K.; Werner, H. J. *Chem. Phys. Lett.* **1992**, *190*, 1.

(24) Langhoff, S. R.; Partridge, H.; Bauschlicher, C. W., Jr. *Chem. Phys.* **1991**, *153*, 1.

(25) Lee, T. J.; Taylor, P. R. *Int. J. Quantum Chem. Symp.* **1989**, *23*, 199. Lee, T. J.; Rendell, A. P.; Taylor, P. R. *J. Phys. Chem.* **1990**, *94*, 5463.

(26) LeRoy, R. J. *LEVEL 6.1 − A computer program for solving the radial Schrödinger equation for bound and quasibound levels, and calculating various expectation values and matrix elements.* University of Waterloo Chemical Physics Research Report CP-555R, 1996.

(27) Chamberlain, J. W. *Theory of Planetary Atmospheres*; Academic: New York, 1978.

(28) Yamada, C.; Fujitake, M.; Hirota, E. *J. Chem. Phys.* **1989**, *90*, 3033.

(29) Steinberg, M.; Schofield, K. *J. Chem. Phys.* **1991**, *94*, 3901.

(30) Moore, C. E. *Atomic Energy Levels*; National Bureau of Standards Circular No. 467; US GPO: Washington, DC, 1949.

(31) Neumark, D. M.; Lykke, K. R.; Anderson, T.; Lineberger, W. C. *Phys. Rev. A* **1985**, *32*, 1890.

(32) Müller-Dethlefs, K.; Cockett, M. C. R.; Wright, T. G. *Annu. Rep. Prog. Chem. C* **1998**, *94*, 327.

(33) Soldán, P.; Špirko, V.; Lee, E. P. F.; Wright, T. G. To be published.

(34) Lee, E. P. F.; Soldán, P.; Wright, T. G. *Chem. Phys. Lett.* **1998**, *295*, 354.