Ab Initio Characterization of Several States of Nitroxylium (NO_3^+). Comparison of Fragmentation Energies of Nitroxylium, Nitroxyl (NO_3), and Nitrate

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Ab initio calculations have been performed at the self-consistent field (HF) level, and its perturbative extensions up to fourth-order (MPn), for several electronic states of nitroxylium (NO_3^+) as well as for a large number of reference species. Geometries are optimized at the HF/DZ and HF/DZP levels (double zeta and double zeta plus polarization bases). The ground state is found to be the D_{3h} $^1A_1'$ state, with the C_{2v} $^1A_1$ (closed Y) state higher by 0.94 eV. The relationship between adding electrons or oxygen atoms to NO^+ and NO_2^+ is explored, especially in relation to fragmentation energies of NO_3^{+q} ($q = 0$ or 1). A comparison is drawn between NO_3^+ and two isoelectronic species, CO_3 and $C(CH_2)_3$, where no surprises are found.

INTRODUCTION

To our knowledge no previous work has been done on the nitroxylium ion, NO_3^+, which is not surprising as this species is expected to be metastable. However, characterization of NO_3^+ is important in that an analysis of this characterization, in the context of the NO_3^-, NO_3, NO_3^+ progression, can provide additional insight into the atmospherically important nitroxy radical, NO_3, as well as an interesting comparison to the isoelectronic species CO_3 and $C(CH_2)_3$, the latter of which having been extensively discussed in the literature.[1-3]

COMPUTATIONAL DETAILS

Ab initio energies and wave functions were computed for NO_3^+ and a large number of reference species, namely NO_3, NO_3^-, NO_2^+, NO_2, NO_2^-, NO^+, NO, NO^-, O_2^+, O_2, O_2^-, O^+, O, and O^- using the Gaussian 86 program,[4] thus complementing our earlier studies[5-6] of NO_3. The levels of approximation used include self-consistent field (HF), second-order Moeller–Plesset perturbation theory with single and double excitations (MP2), third-order Moeller–Plesset with single and double excitations (MP3), and fourth-order Moeller–Plesset with single, double, triple, and quadruple excitations (MP4SDTQ). In all cases excitations from core orbitals were excluded. The double zeta[7] (DZ), DZ plus polarization (DZP), and DZP plus diffuse functions (DZ + P) bases of Huzinaga with Dunning's recommended contraction (4s, 2p,

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1d)[8a] were used. (The polarization sets[8b] add six functions per atom, and the diffuse functions[8c] four.) Geometries were optimized at the HF/DZ and the HF/DZP levels using analytic gradients, while vibrational frequencies were calculated at the HF/DZ level using analytic second derivations.

RESULTS AND DISCUSSION

General

We have computed energies and geometries for the ground states of NO_3^+, NO_3, NO_3^-, NO_2^+, NO_2, NO_2^-, NO^+, NO, NO^-, O_2^+, O_2, O_2^-, O^+, O, and O^- (Tables I–V). For NO_3^+ we located, and verified by analytic frequency calculations, a total of seven Y-shaped (D_{3h} and C_{2v} symmetries) local minima (Fig. 1 and Table I), namely $^1A_1'$ (D_{3h}, open Y), $^1A_1$(C_{2v}, closed Y), $^3B_2$(C_{2v}), $^3A_2'$(D_{3h}, 4π), $^3A_1$(C_{2v}) and a pair of $^3B_1$(C_{2v}) states, where the higher energy $^3B_1$ state probably has a wave function correlating in D_{3h} to a broken symmetry counterpart of the $^3A_2''$ state. We have also located six other local stationary points on this surface, namely $^1A_1$ (four-membered ring), $^3A_2'$(D_{3h}, 6π), $^3A_2''$(D_{3h}, 7π), $^1A_1$(4π), and a pair of $^3A_2$ states where the lower $^3A_2$(C_{2v}) state probably has a wave function correlating in D_{3h} to a broken symmetry counterpart of the $^3A_1''$ state. Furthermore we have followed four more states out to their dissociated limits, namely $^3B_1$ and $^3A_2$, which both dissociate to NO_2^+($^1\Sigma_g^+$) + $O(^3P)$, plus $^1A_1$(4π) and a butadiene-like $^1A'$(C_s) state, which both dissociate to NO_2^+ ($^1\Sigma_g^+$) + $O(^1S$ or ^1D). The latter pair of these implies that NO_2^+ is an effective quencher of the 5577 Å emission of O.

Table I specifically includes optimized geometries for NO_3^-, NO_3, and NO_3^+, information about the elec-

Table I. Geometries[a] and spin expectation values for NO_3^{+q}

Species	Symmetry	State	SOMO[b]	R1(Å)	R2(Å)	A(deg)	S(S + 1)[c]
NO_3^-	D_{3h}	$^1A_1'$	none	1.231	1.231	120.0	0.0
NO_3	D_{3h}	$^2A_2'$	b_2	1.203	1.203	120.0	0.788
	C_{2v}	$^2B_2$	b_2	1.180	1.337	114.2	0.807
	C_{2v}	$^2B_1$	b_1	1.182	1.376	115.1	0.758
NO_3^+	D_{3h}	$^1A_1'$	none	1.185	1.185	120.0	0.0
				(1.232)	(1.232)	(120.0)	
	C_{2v}	$^1A_1$	none	1.116	1.277	144.0	0.0
				(1.143)	(1.356)	(144.5)	
	C_{2v}	$^3B_2$	$a_1 + b_2$	1.162	1.316	122.9	2.708
				(1.268)	(1.401)	(121.3)	
	D_{3h}	$^3A_2'$	$b_1 + a_2$	1.265	1.265	120.0	2.479
				(1.325)	(1.325)	(120.0)	
	C_{2v}	$^3B_1$	$a_2 + b_2$	1.312	1.242	118.4	2.592
				(1.381)	(1.309)	(118.9)	
	D_{3h}	$^3A_2'$	$a_1 + b_2$	1.258	1.258	120.0	2.077
				(1.314)	(1.314)	(120.0)	
	C_{2v}	$^1A_1$ [d]	none	1.863	1.243	47.54	0.0
				(1.974)	(1.282)	(48.56)	
	C_{2v}	$^3B_1$ [d]	$a_2 + b_2$	1.197	1.284	131.8	2.908
				(1.276)	(1.336)	(129.8)	
	D_{3h}	$^3A_2''$ [d]	$a_1 + 2b_2 + b_1$	(1.422)	(1.422)	(120.0)	3.189
	C_{2v}	$^3A_1$ [d]	$b_2 + b_2$	(1.370)	(1.242)	(122.4)	2.067
	C_{2v}	$^3A_2$ [d]	$b_1 + b_2$	(1.406)	(1.237)	(121.8)	2.130
	C_{2v}	$^3A_2$ [d]	$a_1 + a_2$	(1.385)	(1.325)	(118.0)	2.960
	C_{2v}	$^1A_1$ [d]	none	(1.196)	(1.322)	(127.7)	0.0

[a]In order of ascending energies (Tables III–V). Values in parenthesis are at the HF/DZ level. Values are not in parenthesis, at the HF/DZP level.

[b]Singly occupied molecular orbital. The notation is for the C_{2v} group.

[c]Units of $(h/2\pi)^2$.

[d]The HF/DZ and HF/DZP energies are available upon request.

tronic configuration, spin expectation values, and HF energies for those states of NO_3^+ we decided not to pursue any further. The configurations studied in this work are: (1) a configuration for each of the seven triplets which arise from eight electrons in the $(1e'')$, $(4e')$ and $(1a_2')$ orbitals; (2) the closed shell singlets; $\ldots$ $(1e'')^4(1e')^4(1a_2')^0$, two times $\ldots$ $(1a_2)^2(2b_1)^2$-$(8a_1)^2(4b_2)^2(5b_2)^0$, $\ldots$ $(2b_1)^2(8a_1)^2(4b_2)^2(5b_2)^2(1a_2)^0$, $\ldots$ $(1a_2)^2(8a_1)^2(4b_2)^2(5b_2)^2(2b_1)^0$, and a C_s configuration with four pi electrons, where the last two dissociate

to NO_2^+ + O; (3) a somewhat odd configuration, $\ldots$ $(1e'')^4(4e')^2(1a_2')^1(2a_2'')^1$. (See Van de Guchte et al.[9] for an excellent discussion of the configurations which are likely to play a significant role in the valence space of Y shaped CO_3, or NO_3^+.) Table II contains the same information as Table I but for the fragments of the species reported in Table I. In the cases of NO^{+q} + O_2^{+p} (where p and q are equal to zero or one) the combined configurations all have at least one more pair of electrons in a_1 orbitals than

Table II. HF/DZP geometries and spin expectation values for the fragments of the NO_3^{+q} systems.

Species	State	SOMO[a]	R(Å)	A(deg)	S(S + 1)[b]
O^-	^2P	a_1, b_1, or b_2	—	—	0.754
O	^3P	a_1, b_1, or b_2	—	—	2.007
O^+	^4S	$a_1 + b_1 + b_2$	—	—	3.755
NO^-	$^3\Sigma$	$b_1 + b_2$	1.255	—	2.034
NO	$^2\Pi$	b_1 or b_2	1.133	—	0.773
NO^+	$^1\Sigma$	none	1.045	—	0.0
O_2^-	$^2\Pi_g$	a_2 or b_2	1.300	—	0.771
O_2	$^3\Sigma_g^-$	$a_2 + b_2$	1.172	—	2.039
O_2^+	$^2\Pi_g$	a_2 or b_2	1.080	—	0.761
NO_2^-	$^1A_1$	none	1.233	116.6	0.0
NO_2	$^2A_1$	a_1	1.169	135.8	0.767
NO_2^+	$^1\Sigma_g$	none	1.096	180.0	0.0

[a]Singly occupied molecular orbital. The notation is for the C_{2v} group assuming fragment orientations as shown in Figure 1.

[b]Units of $(h/2\pi)^2$.

Table III. *Ab initio* energies for the NO$_3^+$ system.

Species	State	HF/DZP	MP2/DZP	MP3/DZP	MP4SDTQ/DZP
NO$^+$ + O$_2$	$^1\Sigma$ + $^3\Sigma_g^-$	−278.59513	−279.22947	−279.23294	−279.26358
NO$_2^+$ + O	$^1\Sigma_g^+$ + ^3P	−278.52716	−279.15560	−279.13036	−279.19292
NO + O$_2^+$	$^2\Pi$ + $^2\Pi_g$	−278.47974	−279.12195	−279.11058	−279.15566
NO$_2$ + O$^+$	$^2A_1$ + ^4S	−278.44566	−279.01747	−279.01116	−279.05826
NO$_3^+$ (D$_{3h}$)	$^1A_1'$	−278.27975	−279.15522	−279.03544	−279.17420
NO$_3^+$ (C$_{2v}$)	$^1A_1$	−278.39124	−279.10413	−279.08058	−279.13954
NO$_3^+$ (C$_{2v}$)	$^3B_2$	−278.47269	−279.04414	−279.06138	−279.10206
NO$_3^+$ (D$_{3h}$)	$^3A_2'(4\pi)$	−278.49993	−279.03366	−279.06073	−279.09448
NO$_3^+$ (C$_{2v}$)	$^3B_1$	−278.48887	−279.03122	−279.05618	−279.09432
NO$_3^+$ (D$_{3h}$)	$^3A_2'(6\pi)$	−278.25383	−279.00825	−278.96889	−279.05817

[a]Energies in au (hartrees).
[b]All values at HF/DZP geometries (Tables I and II).

any of the states of NO$_3^{+q}$. The energies of all these states are listed in Tables III–V.

Table VI reports electron affinities (EA) and ionization energies (IP) for NO$_3$, NO$_2$, NO, O$_2$, and O. For EA ab initio values were computed at the MP4SDTQ level, first by doing single point energy calculations at HF/DZP geometries and using the DZP basis, then by doing single point energy calculations at the DZP geometry, but using the DZ + P basis. The difference between these two methods ranges from 1.06 eV for O, to 0.35 eV for NO$_3$, which is symptomatic of an inherent error due to size inconsistency that decreases as the size of the basis is increased.[10-12] In no case did we make an effort to correct this problem further as we focus on the order of EA and IP, rather than absolute predictions. We also did not correct for zero-point energies as this correction is expected to be small,[13,14] however we did check this assumption for NO$_3$ where the correction amounts to −0.03 eV using experimental[15-18] frequencies, or +0.07 eV using calculated[5] harmonic frequencies.

The absolute errors in EA, at the ΔMP4SDTQ/ DZ + P level, are roughly 0.20 eV for the molecular species and 0.50 eV for O, but differences between these predictions are expected to be in error by less than 0.10 eV for molecule-molecule comparisons to nearly 0.25 eV for molecule-atom comparisons. For

IP the size inconsistency error is not quite as large, therefore we chose to forego DZ + P calculations. However, the correction for the zero point energy in the case of NO$_2 \rightarrow$ NO$_2^+$ is likely significant and positive, as the cation has four vibrational degrees of freedom compared to three in the neutral. At the ΔMP4SDTQ/DZP level our residual errors in IP range from 0.15 eV for O$_2$ to 0.70 eV for O, and differences between these predictions are off by less than 0.20 eV for molecule-molecule comparisons to nearly 0.50 eV for molecule-atom comparisons. Based on this we would expect the true IP of NO$_3$, for which there is no experimental data, to be 11.75 ± 0.05 eV.

Table VII is a repeat of Table VI with the roles of atomic oxygen and one electron permuted. We see the "oxygen affinities" (OA) are 0.26 ± 0.04 eV larger than corresponding EA, while "oxygen detachment energies" (ODE) are 6.53 ± 0.04 eV smaller than corresponding IP. What is striking about OA and ODE is the fact that differences amongst OA are nearly identical to differences amongst EA, and differences amongst ODE are nearly identical to differences amongst IP (in two of six cases rigorously identical). Table VIII is a tabulation of these relative EA, IP, OA, and ODE values, all at the ΔMP4SDTQ/DZP level. If one further adjusts these energy differences by the differences in zero-point energies one notices that oxygen becomes even more analogous to an electron

Table IV. *Ab initio* energies[a,b] for the NO$_3$ system.

Species	State	HF/DZ + P (HF/DZP)	MP2/DZ + P (MP2/DZP)	MP3/DZ + P (MP3/DZP)	MP4SDTQ/ DZ + P (MP4SDTQ/DZP)
NO + O$_2$	$^2\Pi$ + $^3\Sigma_g^-$	−278.94081 (−278.93485)	−279.57046 (−279.55525)	−279.56903 (−279.55530)	−279.60993 (−279.59390)
NO$_2$ + O	$^2A_1$ + ^3P	−278.89064 (−278.88567)	−279.50549 (−279.49080)	−279.49882 (−279.48540)	−279.54904 (−279.53289)
NO$_3$(D$_{3h}$)	$^2A_2'$	−278.84929 (−278.83599)	−279.58437 (−279.56996)	−279.54461 (−279.53154)	−279.61335 (−279.59702)
NO$_3$(C$_{2v}$)	$^2B_2$	(−278.88679)	(−279.54520)	(−279.53577)	(−279.58484)
NO$_3$(C$_{2v}$)	$^2B_1$	(−278.86923)	(−279.52735)	(−279.51973)	(−279.56577)

[a]Energies in au (hartrees).
[b]All values at HF/DZP geometries (Tables I and II).

Table V. *Ab initio* energies[a-b] for the NO_3^- system.

| Species	State	HF/DZ+P (HF/DZP)	MP2/DZ+P (MP2/DZP)	MP3/DZ+P (MP3/DZP)	MP4SDTQ/DZ+P (MP4SDTQ/DZP)
$NO^- + O_2$	$^3\Sigma + {}^3\Sigma_g$	-278.93272	-279.56452	-279.56585	-279.60505
		(-278.91295)	(-279.52923)	(-279.53386)	(-279.56782)
$NO_2^- + O$	$^1A_1 + {}^3P$	-278.94820	-279.58212	-279.57972	-279.62658
		(-278.92995)	(-279.54438)	(-279.54715)	(-279.58632)
$NO + O_2^-$	$^2\Pi + {}^2\Pi_g$	-278.91196	-279.57580	-279.57162	-279.61658
		(-278.89168)	(-279.53972)	(-279.53932)	(-279.57768)
$NO_2 + O^-$	$^2A_1 + {}^2P$	-278.86872	-279.54336	-279.52959	-279.58486
		(-278.83872)	(-279.49193)	(-279.48295)	(-279.53013)
$NO_3^- (D_{3h})$	$^1A_1'$	-279.00186	-279.71844	-279.69843	-279.74938
		(-278.99091)	(-279.69138)	(-279.67498)	(-279.71974)

[a]Energies in au (hartrees).
[b]All values at HF/DZP geometries (Tables I and II).

in this context. Furthermore, this analogy holds independent of basis set size. In other words the energy of (NO_3 + NO^- + NO_2^+) nearly equals that of (NO_2^- + NO_3^+ + NO).

Figures 2–4 display graphically the differences between $NO_3^{\pm q}$ (dashed lines) and their most reasonable fragments (solid lines), where size inconsistency again shows up. Therefore, the large molecules are expected to lie somewhat lower than depicted ($NO_2^{\pm q}$ < $NO_2^{\pm q}$ + $O^{\pm p}$ < $NO^{\pm q}$ + $NO^{\pm p}$). Figure 2 is especially interesting as it graphically points out the wildly erratic behavior of the (open Y) $^1A_1'$ state of NO_3^+ which crosses five other states over a three eV energy range upon going from MP2 to MP3, then re-

crosses all of them upon going to MP4SDTQ. The only other crossover seen at these levels in these figures is with the $^2A_2'$ of NO_3, which crosses and recrosses two other states over a one eV energy range, and because of this similarity we expected to see (where possible) some of the same instabilities[18] in the $^1A_1'$ wave function (WF) as we saw[5] in the $^2A_2'$ WF. (Note: the broken symmetry solution corresponding to $^1A_1'$ is still expected to lie much higher in energy than the closed Y structure at the HF level, which makes it difficult to characterize.) We found the $^1A_1'$ WF has two out of three possible instabilities, namely it is unstable with respect to relaxation to complex space and also with respect to relaxation of the spin restricted, $\langle S(S + 1) \rangle = 0$, constraint. However, it proves impossible to relax the spin constraint on the $^1A_1'$ WF and still maintain its totally symmetric character. That is, the spin unrestricted ("UHF") WF is more like $^3B_2$ or $^1B_2$ than it is like $^1A_1'$.

Figure 5 brings Figures 2–4 together so that one
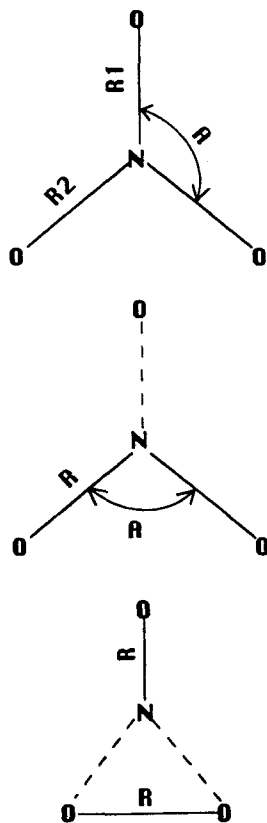
Figure 1. Definition of structural parameters.

Table VI. Electron affinities and ionization energies.[a]

Species	MP4/DZP[b]	MP4/DZ+P[c]	Experimental
Electron	affinities		
NO	-0.71	-0.13	0.04^d
NO_2	1.46	2.11	2.28^e
NO_3	3.34	3.70	3.92^f
O_2	-0.44	0.18	0.44^g
O	-0.08	0.98	1.46^h
Ionization	energies		
NO	8.99	—	9.26^i
NO_2	9.25	—	9.59^j
NO_3	11.51	—	—
O_2	11.92	—	12.07^g
O	12.92	—	13.62^g

[a]In eV.
[b]ΔMP4SDTQ/DZP//HF/DZP values.
[c]ΔMP4SDTQ/DZ+P//HF/DZP values.
[d]reference 27.
[e]reference 30.
[f]reference 26.
[g]reference 28.
[h]reference 29.
[i]reference 31.
[j]reference 32.

Table VII. Oxygen affinities and detachment energies.[a]

| Species | Oxygen affinities | | Oxygen detachment energies | |
	MP4/DZP[b]	MP4/DZ+P[c]	MP4/DZP[b]	MP4/DZ+P[c]
NO$_2^+$	−0.51	—	2.49	—
NO$_2$	1.75	1.76	2.74	2.79
NO$_2^-$	3.63	3.34	4.92	5.03

[a]In eV.
[b]ΔMP4SDTQ/DZP//HF/DZP values.
[c]ΔMP4SDTQ/DZ+P//HF/DZP values.

can easily examine the thermochemistry of this system. For example, one sees that recombination of an electron to NO$_3^+$ can proceed to four possible products, namely NO$_3$, NO + O$_2$, NO$_2$ + O, and NO$_2^+$ + O$^-$. Also, one clearly sees that any system which includes only neutrals or anions is much lower than any system that includes a cation, while only nitrate is clearly lower than the neutrals. In other words, it is easy to see that the NO$_3$ moiety is strongly destabilized with respect to its fragments as electrons are taken away.

Comparison to Isoelectronic Counterparts

As expected the same order of the first few states is seen[9] for CO$_3$ and NO$_3^+$, namely $^1A_1'$ (open Y) < $^1A_1$ (closed Y) < $^1A_1$ (ring) < triplets. However, the order of the low lying triplets is somewhat different. For NO$_3^+$ it is $^3B_2$ < $^3A_2' \approx {}^3B_1$, while[9] for CO$_3$ it is $^3B_1$ < $^3A_2'$ with $^3B_2$ not having been considered.

For C$_4$H$_6$ the open structure (butadiene) and the ring structure (cyclobutene) are clearly lower in energy than the Y shaped structures, but this is not a fair extension as the hydrocarbons can have a hydrogen migrate so that each carbon has eight electrons around it, while CO$_3$ and NO$_3^+$ cannot. The comparison is fair for trismethylenemethane, C(CH$_2$)$_3$, where one can clearly predict the pertinent states by rotating zero, one, two or three methylene groups perpendicular to the plane of the carbon skeleton. For the planar molecule only three states: $^3A_2'(4\pi)$, $^1A_1'(4\pi)$ and $^1E'(4\pi)$ are reasonable, of which the triplet is lowest. (For a nonplanar D_{3h} structure the set of 7π states, arising from four electrons in the e', a_2' and a_2'' orbitals, are reasonable, which is

where the previously dubbed odd configuration of NO$_3^+$ comes from. We considered the $^3A_2''$ state.) Rotating one methylene group, we expect $^1B_1$ or $^3B_1$ to be important. Rotating two methylene groups, we expect C(CH$_2$)$_3$ to collapse into methylenecyclopropane, $^1A_1$ (closed Y). Indeed, most of the literature[1–3] relates to at least one of these states, and from it one can clearly deduce the order of these states: $^1A_1(6\pi) < {}^3A_2'(4\pi) < {}^1B_1$ (or $^3B_1(5\pi)$). The same order is seen for NO$_3^+$, at MP2 and higher levels. However, the difference between $^3A_2'$ and $^3B_1$ in NO$_3^+$ is only 4.3 meV at the MP4SDTQ level.

Van de Guchte et al.[9] show that $^1A_1'$ (open Y) of CO$_3$ is lower than $^1A_1$ (closed Y) by 0.33 eV at the CI/DZP[19] level. However, they neglected to consider triple and quadruple excitations, which respectively add 1.90 and −1.40 eV to this energy difference at the ΔMP4 level for NO$_3^+$. We calculated the $^1A_1$(closed Y) − $^1A_1'$(open Y) energy difference for NO$_3^+$ at the RHF, RMP2, RMP3, and RMP4SD levels, where the "R" refers to spin restricted. Values of −3.03, 1.39, −1.23, and 0.44 eV were found respectively. We then repeated these calculations at the UHF, and UMP2 levels. Values of 0.55 and −1.26 eV were found respectively. (Note: the UHF solution for the $^1A_1$ WF is scarcely $^1A_1'$ at all.) For these reasons we are inclined to believe that $^1A_1'$ lies below $^1A_1$ even though the perturbative series is far from converging.[20] We also believe $^3B_2$ is the lowest triplet (Fig. 2 and Table III). For both the ground state triplet and the ground state singlet no immediately analogous state exists for trismethylenemethane. In fact, it is surprising that $^3B_2$ exists as a local minimum on the NO$_3^+$ surface as its configuration $(\ldots(8a_1)^1(5b_2)^1)$ is conducive to free dissociation, much like one of the $^3B_1$ states $(\ldots(8a_1)^1(2b_1)^1$, that we followed out to NO$_2^+$ + O.

Table VIII. *Relative* affinities and detachment energies.[a,b]

Species	EA (NO$_x$)	OA[c] (NO$_2^{+q}$)	IP (NO$_x$)	ODE[c] (NO$_2^{+q}$)
NO or NO$_2^+$	−2.16	−2.26[d]	0.00	0.00
NO$_2$	0.00	0.00	0.26[d,e]	0.26[d,e]
NO$_3$ or NO$_2^-$	1.88[e]	1.88[e]	2.53	2.43[d]

[a]In eV with EA and OA relative to NO$_2$, and IP and ODE relative to NO and NO$_2^+$ respectively.
[b]ΔMP4SDTQ/DZP//HF/DZP values.
[c]Atomic oxygen analog to electron affinities and ionization energies.
[d]Zero-point energy correction is signficant and positive.
[e]These pairs of relative energy differences are rigorously identical.
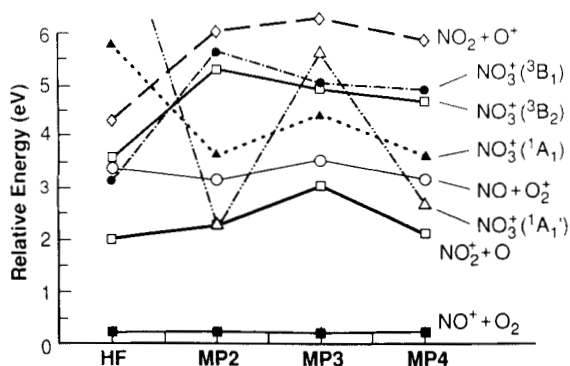
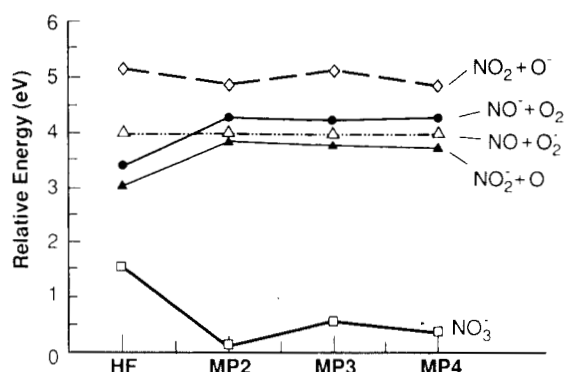**Figure 2.** Energies in eV for the NO_3^+ system relative to $NO^+ + O_2$. All values at HF/DZP optimized geometries.

Reanalysis of Nitroxyl

As with previous articles[5,6] we have chosen to study NO_3 because of its widespread impact on atmospheric processes and because of the computational challenging problem it presents. Our first article included MP4SDTQ/DZP//HF/DZP energies for nine local minima. An important aspect of that work and earlier work[21-23] was the implication that the strong absorption observed at 1.87 eV is likely due to a $^2A_2' \rightarrow {}^2E'$ transition. However, we raised the possibility that this transition may be the second lowest transition of its kind, with the lowest being somewhere between 0.65 and 1.03 eV. (The lower bound is based on the adiabatic energy difference of Davy et al.[24] between $^2A_2'$ and $^2B_2$.)

We now have evidence suggesting that possibility is not correct. The arguments are now presented. (1) The highest occupied molecular orbital (HOMO) of NO_3^- has a_2' character. The difference in orbital energies between this orbital and the highest occupied e' oribtal is much greater than 1.03 eV. (2) The lowest unoccupied molecular orbital (LUMO) of ground state MP4SDTQ level NO_3^+ ($^1A_1'$) is a_2'. If we suppose the existence of a $^2E'$ state of NO_3 which is less than 1.03 eV above $^2A_2'$ then clearly there should be low lying states of NO_3^+, which arise from ($e' \times a_2'$) or ($e' \times e'$) or ($e' \times e''$), within 1.03 eV of the $^1A_1'$ (open
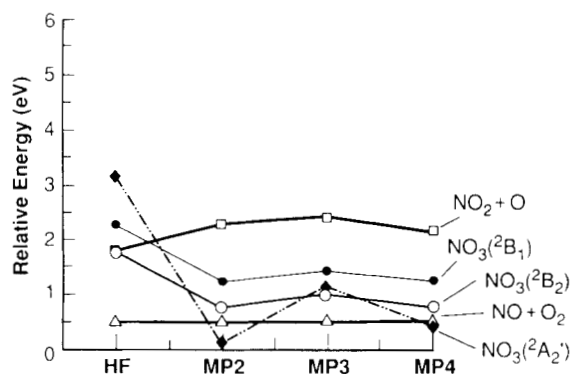
Figure 3. Energies in eV for the NO_3 system relative to $NO + O_2$. All values at HF/DZP optimized geometries.

**Figure 4.** Energies in eV for the NO_3^- system relative to $NO + O_2^-$. All values at HF/DZP optimized geometries.

Y) ground. This is not the case. The triplet states of NO_3^+ all lie at least 1.96 eV above ground, at the MP4SDTQ level, and $^1A_1$ (closed Y) lies 0.94 eV above ground even though it is stabilized by the formation of an oxygen-oxygen single bond.

We also reiterate that the previously[5,24] characterized $^2B_2$ state could very well be thermally significant. The nitroxy radical, as distinct from NO_3^- and NO_3^+, is strongly influenced by the symmetry allowed reaction between O and NO_2, where the fragments are higher than NO_3 by nearly 1.76 eV, an amount which would compose a conservative estimate of the strength of a nitrogen-oxygen single bond (typically 1.81 to 1.82 eV.)[25] If we suppose the reaction proceeds directly from fragments to D_{3h} (and that a single bond is formed), then we could be left with any one of three states; $^2E''$ or $^2E'$ or $^2A_2'$. However, the reaction may not proceed all the way to D_{3h}, so we expect to see any of three C_{2v} states; $^2B_1$ or $^2B_2$ or $^2B_2$, where the lower $^2B_2$ traces forward to $^2A_2'$.

In light of this additional insight we also expect the A branches of E' and E'' to offer a much better depiction of the spectroscopic states than their corresponding B branches. Thus, according to Kim et al.[23] and the ionization energy of Weaver et al.,[26] we expect to see one band near 4.73 eV and another near 5.82 eV in the photoelectron spectrum (PES) of NO_3^-. The first such excited state band is seen in the PES by Weaver et al.,[26] but they did not look beyond 5.6 eV so could not confirm the well known absorption in the red is one which originates from a D_{3h} ground state.

CONCLUSION

Based on calculations at the MP4SDTQ/DZP//HF/DZP level we expect the ground state of nitroxylium (NO_3^+) to be the D_{3h} $^1A_1'$ state. Higher local minima include a closed Y shaped $^1A_1$ state at 0.94 eV and an open Y shaped $^3B_2$ state at 1.96 eV. However, NO_3^+ is not stable with respect to fragmentation forming $NO^+ + O_2$ nor with respect to fragmentation
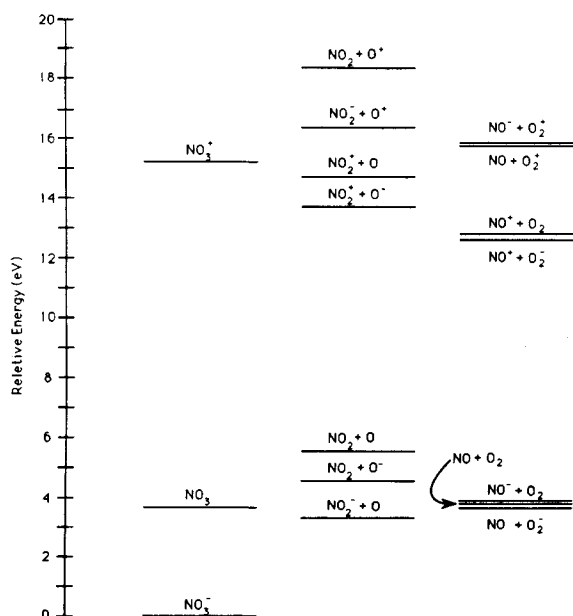
Figure 5. All energies in eV relative to NO_3 . ΔMP4SDTQ/ DZ + P values for anion-neutral differences and ΔMP4SDTQ/ DZP values for cation-neutral differences. The negative sign of EA for NO is wrong.

forming NO_2^+ + O. Exothermicities of these two channels are calculated to be 2.43 and 0.51 eV respectively. The effect on fragmentation energies of adding one or two electrons to NO_3^+ is as follows: For NO_3 the $^2A_2'$ D_{3h} ground state is more stable than NO + O_2 by 85 meV, and more stable than NO_2 + O by 1.76 eV, while NO_3^- is more stable than NO^- + O_2 by 3.93 eV, and more stable than NO_2^- + O by 3.34 eV. A comparison is made between NO_3^+ and two of its isoelectronic counterparts, CO_3 and $C(CH_2)_3$. As expected, NO_3^+ CO_3 have nearly identical properties, while those of $C(CH_2)_3$ are significantly different because of the formation of strong C—H bonds. Still, $C(CH_2)_3$ is similar to NO_3^+ in the sense that closed shell singlets are clearly lower in energy than triplets.

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