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Thermodynamics of $NO^+ \cdot N_2$: Atmospheric Relevance

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The $NO^+ \cdot N_2$ cationic complex is studied using high-level ab initio calculations. The geometry is found to be a skewed T shape, with two linear stationary points corresponding to the $N-O^+ \cdot N-N$ and $N-N \cdot N-O^+$ configurations. At the highest level of theory, CCSD(T)/aug-cc-pVQZ//CCSD(T)/aug-cc-pVTZ, the interaction energy is estimated to be 1950 cm^{-1} (5.6 kcal mol^{-1}), from which a ΔH^{298} interaction enthalpy value of 4.9 kcal mol^{-1} was derived. By using the well-established heat of formation of NO^+, it was possible to derive a standard ΔH_f^{298} value of 230.4 kcal mol^{-1} for $NO^+ \cdot N_2$. In addition, the enthalpy, entropy, free energy and equilibrium constants were calculated for the dissociation of the complex, as a function of altitude, for the earth's atmosphere.

I. Introduction

The $NO^+ \cdot N_2$ cationic complex has been inferred as being the nascent complex formed in the chain of chemical reactions that lead from NO^+ to the protonated water clusters, $H^+(H_2O)_n$, in the ionosphere.[1] The sequence of reactions is potentially very complicated,[2,3] involving complexes consisting of NO^+ interacting with one or more atmospheric ligands, such as H_2O, CO_2, N_2, O_2, and O. At some point, the NO^+ complex rearranges and yields a protonated water cluster, plus products. For example,

$$NO^+ \cdot (H_2O)_n + H_2O \rightarrow [NO^+ \cdot (H_2O)_{n+1}]^* \rightarrow H^+(H_2O)_n + HONO \quad (1)$$

For the NO^+ complexes where water is the only ligand, the critical value of n has been shown to be 3 from unimolecular fragmentation studies,[4] but 4 from laser fragmentation studies;[5] this discrepancy has been discussed very recently.[6]

The suggestion that $NO^+ \cdot N_2$ is the first complex ion to form, despite the fact that the binding energy of $NO^+ \cdot H_2O$ is greater than that of $NO^+ \cdot N_2$, is due to the greater prevalence of N_2 versus H_2O in the upper atmosphere.[1] To calculate accurately the equilibrium constant for the process

$$NO^+ \cdot N_2 \rightarrow NO^+ + N_2 \quad (2)$$

it is desirable to know the binding energy of $NO^+ \cdot N_2$ accurately. Various reports of the binding energy of $NO^+ \cdot N_2$ have been reported, both experimental[1,7−9] and theoretical.[9−11]

Recently, we used MP4 single-point calculations at MP2-optimized geometries (MP4//MP2) to calculate the binding energies and ligand-switching enthalpy changes for the 1:1 $NO^+ \cdot X$ complexes ($X = H_2O$, N_2, and CO_2).[12] The main aim of that work was to generate reliable thermodynamic quantities (enthalpies, entropies, and free energies) from the ab initio data, but to attempt to keep the calculations as inexpensive as possible. For the first time, a consistent level of theory was used for the three complexes, which allowed the calculation of thermodyamical quantities for the ligand-switching reactions, in addition to the calculation of the binding energies for the three complexes.

It is the aim of the present work to calculate the geometry, binding energy, and thermodynamics of the $NO^+ \cdot N_2$ cationic complex at higher levels of theory than those used in ref 12 and to compare the two sets of data. In addition, the linear stationary points on the $NO^+ \cdot N_2$ surface are characterized.

II. Theoretical Methods

The equilibrium geometry of the $NO^+ \cdot N_2$ complex was fully optimized at the MP2/aug-cc-pVDZ, QCISD/aug-cc-pVDZ, and MP2/aug-cc-pVTZ levels of theory where the frozen core approximation was used in each case. In addition, harmonic vibrational frequencies were calculated. Then, the geometry was partially optimized at the CCSD(T) level of theory (again using the frozen core approximation), where the NO^+ and N_2 bond lengths were fixed at the experimental r_e values of the isolated moieties. At each of the calculated minima, the interaction energy was calculated and corrected for basis set superposition error (BSSE), making use of the full counterpoise (CP)

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TABLE 1: Calculated Equilibrium Geometry, Harmonic Vibrational Frequencies, and Interaction Energies for $NO^+ \cdot N_2$

	r_{NO}/Å	R/Å	r_{NN}/Å	∠ONN/°	∠NNN/°	ω_1/cm^{-1}	ω_2/cm^{-1}	ω_3/cm^{-1}	ω_4/cm^{-1}	ω_5/cm^{-1}	ω_6/cm^{-1}	BSSE/cm^{-1}	ΔE_{CP}/cm^{-1}
MP2/aug-cc-pVDZ	1.0968	2.6587	1.1315	102.6	171.6	91.9	107.8	123.3	161.1	2124.4	2158.5	232.0	1831.7
QCISD/aug-cc-pVDZ	1.0773	2.6992	1.1146	102.7	171.6	91.2	109.1	119.2	157.1	2383.7	2386.0	229.6	1700.0
MP2/6-311G* with diffuse p[a]	1.09	2.67	1.12	101	171.2	107	132	135	161	2155	2177		
MP2/aug-cc-pVTZ	1.0826	2.6437	1.1139	102.2	171.4	98.7	113.6	127.4	158.8	2154.9	2187.9	142.8	1935.4
CCSD(T)/aug-cc-pVTZ	1.0632[b]	2.6611	1.0977[b]	101.9	171.7							138.4	1895.5

[a] From ref 12. [b] Fixed at the experimental value (ref 17).

TABLE 2: Enthalpy of Reaction for the Process $NO^+ \cdot N_2 \rightarrow NO^+ + N_2$[a]

	ΔE_R/ cm^{-1} (kcal mol^{-1})	ΔH_R/ kcal mol^{-1}	ΔH_f^{298} ($NO^+ \cdot N_2$)/ kcal mol^{-1}
CCSD/aug-cc-pVTZ	1784 (5.1)	4.4	230.9
CCSD(T)/aug-cc-pVTZ	1899 (5.4)	4.8	230.6
CCSD/aug-cc-pVQZ	1825 (5.2)	4.6	230.8
CCSD(T)/aug-cc-pVQZ	1950 (5.6)[b]	4.9[b]	230.4[b]

[a] ΔE_R is the total energy change, including BSSE, and is equivalent to the dissociation energy, D_e. [b] Estimated. See text.

correction of Boys and Bernardi.[13] In addition, single-point CCSD(T) calculations were performed at the CCSD(T)/aug-cc-pVTZ-optimized geometry using the CCSD(T)/aug-cc-pVTZ and CCSD/aug-cc-pVQZ methods, where all electrons were correlated. As will be seen, when the frozen core approximation was used, or when all electrons were correlated, an almost identical interaction energy was obtained using the CCSD(T)/aug-cc-pVTZ method, after the full counterpoise correction for BSSE.

The linear $N{-}O^+ \cdot N{-}N$ and $N{-}N \cdot N{-}O^+$ configurations represent saddle points on the $NO^+ \cdot N_2$ potential energy hypersurface and arise from internal rotation. The same geometry optimizations were performed as on the minimum.

Analytic derivatives were used to characterize the stationary points found, except for the constrained optimizations performed at the CCSD(T) level.

All MP2 and QCISD calculations were performed employing *Gaussian 94*,[14] and the CCSD and CCSD(T) calculations were performed using MOLPRO.[15]

III. Results and Discussion

Minimum. The optimized geometry and harmonic vibrational frequencies, calculated in the present work for the minimum, are presented in Table 1. As may be seen, the geometry is somewhat insensitive to the level of theory, indicating that these results, and those reported in ref 12, should be reliable. The most accurate intermolecular parameters are probably those at the CCSD(T) level using the aug-cc-pVTZ basis set, where the NO^+ and N_2 bond lengths were frozen to the experimental values. (At the QCISD/QCISD(T) and CCSD/CCSD(T) levels the NO^+ bond length is reproduced very well (see ref 16), and we expect a similar accuracy here.)

The intermolecular vibrational frequencies ($\omega_1-\omega_4$) are also fairly consistent at the different levels of theory (see Table 1), although they differ slightly from those obtained in ref 12. The most noticeable difference is for the intramolecular vibrations, namely the NO^+ stretch (ω_5) and the N_2 stretch (ω_6), which vary by ~200 cm^{-1} at the different levels of theory, but it is expected that the intramolecular vibrational frequencies will be very little changed from the uncomplexed values. The experimental values for the isolated moieties are $\omega_e(NO^+) = 2376.4$ cm^{-1} (ref 17) and $\omega_e(N_2) = 2359.6$ cm^{-1}, which suggests again that the QCISD method is performing well here.

The calculated interaction energies are shown in the final column of Table 1 for the minimum energy structure. As may be seen, the values are fairly consistent at the four levels of theory used, suggesting that a final value of 1900 cm^{-1} (5.4 kcal mol^{-1}) will be close to the true value. To test this further, two more sets of single-point calculations were performed at the CCSD(T) "optimized" geometry. The first were CCSD(T)/aug-cc-pVTZ calculations, where all electrons were correlated: this led to a value of 1899 cm^{-1} for the interaction energy, with a BSSE of 345 cm^{-1}. Note that the use of the frozen core

TABLE 3: Optimized Geometries, Harmonic Vibrational Frequencies, and Interaction Energies for the Linear Saddle Points on the $NO^+{\cdot}N_2$ Potential Energy Hypersurface

	r_{NO}/Å	R/Å	r_{NN}/Å	ω_1/cm^{-1}	ω_2/cm^{-1}	ω_3/cm^{-1}	ω_4/cm^{-1}	ω_5/cm^{-1}	BSSE/cm^{-1}	ΔE_{CP}/cm^{-1}
$N{-}O^+{\cdot}N{-}N$ (R = intermolecular O···N bond length)										
MP2/aug-cc-pVDZ	1.0966	2.8422	1.1314	71.81*i*	85.5	106.8	2117.5	2160.1	184.7	672.3
QCISD/aug-cc-pVDZ	1.0767	2.8887	1.1149	65.8*i*	88.6	99.4	2382.3	2389.1	177.6	677.3
MP2/aug-cc-pVTZ	1.0823	2.8441	1.1137						138.9	737.1
CCSD(T)/aug-cc-pVTZ	1.0632[a]	2.8745	1.0977[a]						139.9	784.2
$N{-}N{\cdot}N{-}O^+$ (R = intermolecular N···N bond length)										
MP2/aug-cc-pVDZ	1.0968	2.9614	1.1314	79.3	87.9*i*	98.7	2120.2	2159.6	185.1	838.0
QCISD/aug-cc-pVDZ	1.0773	2.9825	1.1148	81.8	86.0*i*	96.6	2382.1	2384.8	187.3	754.4
MP2/aug-cc-pVTZ	1.0826	2.9688	1.1138						152.9	906.0
CCSD(T)/aug-cc-pVTZ	1.0632[a]	2.9738	1.0977[a]						158.0	874.0

[a] Fixed at the experimental value (ref 17).

TABLE 4: Calculated Thermodynamics for the Process $NO^+{\cdot}N_2 \rightarrow NO^+ + N_2$ as a Function of Altitude

altitude/ km	T/K	p/Pa	ΔS/J K^{-1}mol^{-1}	ΔH/kJ mol^{-1}	ΔG/kJ mol^{-1}	K_p[a]	K_c/mol dm^{-3}
0	298	101325	79.1	20.5	−3.0	3.4	139.1
0	288	101325	79.4	20.6	−2.2	2.6	107.9
5	256	54050	85.4	20.8	−1.0	0.86	41.1
10	223	26500	92.3	21.1	0.5	0.20	11.0
15	217	12110	99.0	21.1	−0.4	0.15	8.3
20	217	5529.0	105.5	21.1	−1.8	0.15	8.3
25	223	2549.0	111.8	21.1	−3.7	0.19	10.5
30	227	1197.0	117.9	21.0	−5.7	0.25	13.2
35	237	574.6	123.7	21.0	−8.4	0.39	20.2
40	250	287.1	129.1	20.9	−11.4	0.68	33.3
45	264	149.1	134.2	20.8	−14.6	1.2	53.6
50	271	79.78	139.2	20.7	−17.0	1.5	66.7
55	261	42.53	144.7	20.8	−17.0	1.0	48.7
60	247	21.96	150.6	20.9	−16.3	0.60	29.8
65	233	10.93	156.8	21.0	−15.5	0.33	17.1
70	220	5.221	163.3	21.1	−14.8	0.17	9.5
75	208	2.388	170.2	21.2	−14.2	0.089	5.2
80	198	1.052	177.3	21.2	−13.9	0.048	2.9
85	189	0.4457	184.7	21.3	−13.6	0.026	1.7
86	187	0.3734	186.2	21.3	−13.5	0.022	1.5
90	187	0.1836	192.2	21.3	−14.6	0.022	1.5
95	189	0.0760	199.4	21.3	−16.4	0.026	1.7
100	195	0.0320	206.4	21.2	−19.0	0.039	2.4
110	240	0.00710	217.6	21.0	−31.3	0.45	22.8
120	360	0.00254	223.2	20.1	−60.3	14.0	473.2

[a] Note that K_p and K_c are defined at 101325 Pa, and so are only varying with temperature. See text.

approximation led to almost identical values for the interaction energy (1896 cm^{-1}) as when all electrons were correlated (1899 cm^{-1}), at least at the CCSD(T)/aug-cc-pVTZ level of theory; this is true after using the full CP correction (note that the BSSE is significantly smaller when the frozen core approximation is used, as expected). The second method was employing CCSD(T)/aug-cc-pVQZ calculations, where all electrons were correlated: this led to a value of ~1950 cm^{-1}, where the CCSD(T) value was estimated from the CCSD and CCSD(T) values obtained with the aug-cc-pVTZ basis set. This is our best estimate of the binding energy of $NO^+{\cdot}N_2$.

To compare this value to experimental values, it is necessary to correct the interaction energy to a standard enthalpy (ΔH_R), using standard formulas, under the assumptions of an ideal gas and a rigid rotor harmonic oscillator (RRHO). The results of doing this for the forward reaction 2 are shown in Table 2. These may be corrected to ΔH_f^{298} by making use of standard ΔH_f^{298} values: 0 kcal mol^{-1} for N_2 (by definition), and 235.3 ± 0.2 kcal mol^{-1} (ref 18) for NO^+ (note that the stationary electron convention is used in the present work). Thus, our best value for $\Delta H_f^{298}(NO^+{\cdot}N_2)$ is (230.4 ± 0.5) kcal mol^{-1}, where the uncertainty arises from the uncertainty in $\Delta H_f^{298}(NO^+)$ and the estimated error in the ab initio total energy change.

There have been a number of experimental and theoretical determinations of the binding enthalpy of $NO^+{\cdot}N_2$. The values all tend to lie in the range 4−5.5 kcal mol^{-1}, and so there is not great uncertainty surrounding this value, although it is always desirable to have as accurate a value as possible. As noted above, the most reliable value of ΔE_R here converts to a most reliable value for ΔH_R of 4.9 kcal mol^{-1}. This value may be compared to the best value obtained in ref 12 of 4.5 kcal mol^{-1}. Thus, the value here is only ca. 0.4 kcal mol^{-1} higher. This difference appears to be localized in the calculation of the total energy change: the value here is expected to be the more reliable, owing to the use of higher levels of theory and larger basis sets. When compared to previous theoretical and experimental results, very good agreement is obtained, with Zinn et al.[11] obtaining 5.0 kcal mol^{-1} from RHF/6-31+G*//RHF/4-31G calculations and two experimental studies yielding 4.4 kcal mol^{-1} (ref 8) and 4.2 kcal mol^{-1} (ref 1). A value of 5 ± 1 kcal mol^{-1} is recommended.

As far as the entropy is concerned, there appear to be four available experimental values: 15.7 cal K^{-1} mol^{-1} (ref 1), 18.5 cal K^{-1} mol^{-1} (ref 7), 13.3 cal K^{-1} mol^{-1} (ref 8) and 17.0 cal K^{-1} mol^{-1} (ref 9). Comparing these to the calculated value of ΔS^{298} = 18.9 cal K^{-1} mol^{-1} here (see first row of Table 4) indicates that the experimental value of Turner et al. (ref 7) is the most reliable. It also compares reasonably favorably with the value of $\Delta S_{298} = -19.6$ kcal mol^{-1} calculated in ref 12. We recommend a value of ΔS_{298} = 18.5 ± 1.5 cal K^{-1} mol^{-1} at a pressure of 1 atm.

Saddle Points. Table 3 contains the optimized geometries of the two linear saddle points, where the geometry has been constrained to be linear. As may be seen, again, the geometry is rather insensitive to the level of theory, with the vibrational frequencies also being rather insensitive. The calculated energies at the CCSD(T)/aug-cc-pVTZ level indicate that there is an internal rotational barrier of ~ 1025 cm^{-1} on moving to the $N{-}N{\cdot}N{-}O^+$ transition state from the minimum, and a barrier of 1115 cm^{-1} on moving to the $N{-}N{\cdot}O{-}N^+$ transition state (no zero-point energies have been accounted for). This is rather high and would suggest that the thermodynamics will not be affected by the internal rotation to a large degree, and so the values given above, under the RRHO approximation should be reliable. The lower barrier in the $N{-}N{\cdot}N{-}O^+$ orientation is consistent with the lower energy barrier for the Ar atom passing the N end of NO^+ in the $Ar{\cdot}NO^+$ cationic complex.[16] Presumably, this is because of the higher charge on the N atom in NO^+ (at the MP2/aug-cc-pVTZ and QCISD/aug-cc-pVDZ levels, the charge is distributed as $N^{+0.8}{-}O^{-0.2}$, with almost zero charge on N_2), which leads to a greater charge-induced dipole interaction with N_2.

Thermodynamics as a Function of Altitude in the Earth's Atmosphere. These thermodynamics were again calculated assuming an ideal gas and employing the RRHO approximation. The calculated enthalpies, entropies, and free energies of reaction for reaction 2, at the appropriate temperatures and pressures for a particular altitude, are given in Table 4. Also given are values for K_p which, by definition, is not dependent upon the pressure (since it is only defined at the standard pressure, $p^0 = 101325$ Pa) but is dependent upon temperature. This may be converted to K_c, the equilibrium constant defined in terms of concentrations, by multiplying by p^0/RT. (Note that, as for K_p, K_c is independent of pressure.) Both equilibrium constants are given in Table 4.

As may be seen, the equilibrium favors $NO^+ + N_2$ at all altitudes, but that at altitudes between 80 and 95 km, $[NO^+ \cdot N_2]$ is expected to be the highest, assuming reaction 2 is the only process occurring. It is notable that this is precisely the altitude at which the changeover from a dominance of NO^+ ions to $H^+(H_2O)_n$ ions occurs.[3]

IV. Conclusions

The $NO^+ \cdot N_2$ cationic molecular complex has been studied using high-level ab initio calculations. The equilibrium geometry is confirmed to be a skewed T shape, with two linear stationary points lying > 1000 cm^{-1} above this. The interaction energy ($= D_e$) has been calculated to be 1950 cm^{-1} (5.6 kcal mol^{-1}) at the highest level of theory used. This translates to an interaction enthalpy of 4.9 kcal mol^{-1}. Recommended values (at 1 atm pressure) for the dissociation reaction are $\Delta H^{298} = 5 \pm 1$ kcal mol^{-1} and $\Delta S_{298} = 18.5 \pm 1.5$ cal K^{-1} mol^{-1}. The close agreement between the values obtained herein and those from ref 12 suggests that the other values derived therein should be reliable to within the precision quoted here.

The standard heat of formation of $NO^+ \cdot N_2$ is derived as 230.4 kcal mol^{-1}. The entropy, enthalpy, and free energy of formation are calculated as a function of altitude in the earth's atmosphere, and these indicate that the concentration of $NO^+ \cdot N_2$ is expected to be the highest between 80 and 95 km, which is precisely the region where the changeover between $NO^+ \cdot X$ and $H^+(H_2O)_n$ ions occurs, supporting the hypothesis that complexation of NO^+ to N_2 is a first step in the production of protonated water clusters.

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