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Citation: *J. Chem. Phys.* **111**, 3420 (1999); doi: 10.1063/1.479626

View online: <http://dx.doi.org/10.1063/1.479626>

View Table of Contents: <http://jcp.aip.org/resource/1/JCPSA6/v111/i8>

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Structure and potential energy surface for $\text{Na}^+ \cdot \text{N}_2$

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(Received 15 March 1999; accepted 26 May 1999)

Attention is focused on the $\text{Na}^+ \cdot \text{N}_2$ complex as part of a study of Na^+ -containing complexes, which have been implicated in the formation of sporadic sodium layers in the upper atmosphere. The equilibrium structure is found to be linear, in agreement with previous studies. A potential energy hypersurface is calculated at the CCSD(T)/aug-cc-pVTZ level of theory, where the N_2 moiety is held fixed, but a wide range of Jacobi bond lengths and bond angles are sampled. This hypersurface is fitted to an analytic form and from this anharmonic vibrational separations are calculated, and compared to harmonic values. Rovibrational energy levels are also calculated from the fitted hypersurface. The best estimate of the interaction energy, ΔE_e is 2770 cm^{-1} , and $\Delta H_f^{298}(\text{Na}^+ \cdot \text{N}_2) = (136.5 \pm 2.0) \text{ kcal mol}^{-1}$. © 1999 American Institute of Physics. [S0021-9606(99)30632-2]

I. INTRODUCTION

Recently, we have been involved in a detailed *ab initio* study of Na^+ -containing molecules and complexes, and have so far published results for NaO^+ (Refs. 1 and 2), NaO_2^+ (Ref. 3), and $\text{Na}^+ \cdot \text{Rg}$ ($\text{Rg} = \text{He}, \text{Ne}, \text{and Ar}$).^{4,5} In addition, work on $\text{Na}^+ \cdot \text{CO}_2$ and $\text{Na}^+ \cdot \text{H}_2\text{O}$ is nearing completion, and will be published in due course. Here we focus our attention on the $\text{Na}^+ \cdot \text{N}_2$ cationic complex. The $\text{Na}^+ \cdot \text{X}$ complexes ($\text{X} = \text{atmospheric ligand}$) have received renewed interest recently, owing to their implication in the formation of sporadic sodium layers.^{6,7}

The formation of $\text{Na}^+ \cdot \text{N}_2$ complexes has been considered by a number of workers, both theoretically^{6,8,9,10} and experimentally.¹¹⁻¹⁵ The structure of the $\text{Na}^+ \cdot \text{N}_2$ cationic complex has been studied using *ab initio* methods by a number of workers. Ikuta¹⁶ optimized the geometry at the HF/3-21G level, and obtained interaction energies using the MP3/6-31G**/HF/3-21G method. An interaction energy of $7.5 \text{ kcal mol}^{-1}$ was obtained, which compared favorably with the experimental value of 8 kcal mol^{-1} (Ref. 15). Dixon

*et al.*¹⁷ optimized the geometry at the HF level, with a $[6s5p1d]$ basis set for Na^+ , and a triple- ζ basis set for N, and also calculated the vibrational spectrum. The interaction energy was again calculated using the HF-optimized geometry, employing single-point CISD+Q calculations, where the Q indicated the use of the Davidson correction. The interaction energy was calculated to be $6.74 \text{ kcal mol}^{-1}$ at the highest level of calculation, which converted to an enthalpy change of $7.43 \text{ kcal mol}^{-1}$. In a study concentrating more on Cr^+ and Co^+ complexes, Bauschlicher *et al.*¹⁸ also studied the $\text{Na}^+ \cdot \text{N}_2$ complex at the MCPDF level. The basis set used included diffuse functions, optimized for Na^- and $\text{Na}(^2P)$ rather than for Na^+ , with the underlying basis set being a $(19s13p)$ one, optimized for $\text{Na}(^2S)$; this basis set was contracted on the basis of a calculation performed on $\text{Na}(^1S)$. The interaction energy was calculated to be $7.2 \text{ kcal mol}^{-1}$. Finally, Cox and Plane recently reported the geometry and vibrational frequencies calculated at the HF/6-311G* level together with the interaction energy calculated at the MP4(FULL)/6-311G**/HF/6-311G* level of theory; the latter yielded a value of 9 kcal mol^{-1} . It may thus be seen that there is a range of calculated interaction energies ranging from 6.7 to 9 kcal mol^{-1} , and that the vibrational frequencies have only been calculated within the harmonic oscillator model, at the HF level. Note also that none of the previous calculations appear to have considered the basis set superposition error in the calculation of the interaction energy.

The aims of the present work are twofold; (i) to calculate the optimized geometry, harmonic vibrational frequencies

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and interaction energies at high levels of theory, using an appropriate basis set; and (ii) to calculate a potential energy surface from which to extract rovibrational energy levels to assist in the experimental characterization of the complex.

II. CALCULATIONAL DETAILS

The basis sets used in the majority of the calculations were as follows: for N, the standard aug-cc-pVXZ (X=T, Q, and 5) basis sets were used. For Na⁺, we have previously shown⁴ that the standard versions of these basis sets behave rather poorly for Na⁺ when correlated methods are being employed; consequently we use the basis sets reported in Ref. 4, which have been designed to perform well for Na⁺ at the correlated level of theory, and are of the same size and type as the standard aug-cc-pVXZ basis sets. We simply refer to the use of the aug-cc-pVXZ basis set in the following. GAUSSIAN94 (Ref. 19) was used for the optimization of the geometry of Na⁺·N₂ at the MP2/6-311+G(2df), MP2/aug-cc-pVTZ and MP2/aug-cc-pVQZ levels of theory; whereas MOLPRO (Ref. 20) was used for the optimization at the CCSD(T)/aug-cc-pVTZ and CCSD(T)/aug-cc-pVQZ levels of theory. Harmonic vibrational frequencies were calculated at the MP2/6-311+G(2df) and MP2/aug-cc-pVTZ levels of theory, using analytic gradients in GAUSSIAN94.

The interaction energy was calculated from the difference in the total energies of the complex and the uncomplexed moieties, and corrected for basis set superposition error (BSSE) by the full counterpoise method. In addition, single-point calculations were also performed at the CCSD(T)/aug-cc-pVQZ-optimized geometry, up to the CCSD(T)/aug-cc-pV5Z level of theory, in all cases correcting for BSSE.

Finally, thermodynamical quantities were calculated from the rigid-rotor, harmonic oscillator (RRHO) model.

A potential energy surface was calculated at the CCSD(T)/aug-cc-pVTZ level of theory, with the N₂ bond length fixed at the optimized value obtained at the CCSD(T)/aug-cc-pVTZ level of theory. The number of points calculated was 271, with the Jacobi bond distance ranging from 1.7 to 15 Å, and the Jacobi bond angle ranging from 0° to 180°. The potential energy points were then fitted to an analytical hypersurface and anharmonic vibrational spacings and rovibrational energy levels were calculated. (More details of these calculations are presented below.) Note that each point was corrected for basis set superposition error (BSSE) by the full counterpoise correction.²¹

III. RESULTS AND DISCUSSION

A. Optimized geometry and harmonic vibrational frequencies

The optimized geometries at different levels of theory are shown in Table I. As may be seen the optimized geometry at the minimum was found to be a linear structure, in agreement with the previous results: a conclusion also confirmed by the potential energy hypersurface (*vide infra*). Recently, high-level *ab initio* calculations have been presented on the valence isoelectronic species Li⁺·N₂, which was also concluded to have a linear equilibrium geometry.²²

TABLE I. Optimized geometry of Na⁺·N₂ at various levels of theory. (In all optimizations performed in the present work, the 1s orbitals on Na⁺ were kept frozen, except for the MP2/aug-cc-pVTZ calculations where the 1s orbitals on Na⁺ and both N atoms were kept frozen.)

Method	Basis set	$r_{\text{N-N}}/\text{Å}^a$	$R_{\text{Na-N}}/\text{Å}$
HF ^b	3-21G	1.081	2.323
HF ^c	See text	1.069	2.503
HF ^d	6-311G*	1.07	2.50
MCPF ^e	See text	1.098	2.516
MP2	6-311+G(2df)	1.1103	2.4782
MP2	aug-cc-pVTZ	1.1132	2.4575
MP2	aug-cc-pVQZ	1.1072	2.4516
CCSD(T)	aug-cc-pVTZ	1.0990	2.4460
CCSD(T)	aug-cc-pVQZ	1.0972	2.4455

^aThe experimental equilibrium bond length for uncomplexed N₂ is $r_e = 1.0977$ Å.

^bFrom Ref. 16.

^cFrom Ref. 17.

^dFrom Ref. 6.

^eFrom Ref. 18.

It seems clear from the results in Table I that the MP2 method is performing reasonably well. Also shown in Table I are the optimized geometries reported previously; the values indicate that the HF level performs poorly for both $r_{\text{N-N}}$ and $R_{\text{Na-N}}$, when compared to the highest levels of theory used herein. Even the MCPF calculations give a significantly longer $R_{\text{Na-N}}$. Our experience⁴ with Na⁺-containing complexes suggest that it is the basis set of Na⁺ itself that is the most likely cause of this discrepancy.

Employing the CCSD(T) method, the highest level of theory used, it may be seen that the optimized Na⁺-N bond length is very similar using both the aug-cc-pVTZ and aug-cc-pVQZ basis sets, suggesting that the smaller basis set is close to saturation. The N₂ bond length is slightly more demanding, as is well known, but again, is close to saturation here. Note that, since the N₂ vibrational frequency is expected to be far above that of the intermolecular modes, then the N₂ vibration is decoupled from the intermolecular surface, to a good approximation (a similar situation arises for Ar·NO⁺, where the NO⁺ vibration is decoupled from the intermolecular motion of the complex).²³ Overall, the CCSD(T)/aug-cc-pVTZ method is expected to produce an accurate potential energy surface for the Na⁺·N₂ system.

The harmonic vibrational frequencies were calculated at the MP2/6-311+G(2df) and MP2/aug-cc-pVTZ levels of theory in the present work. The values obtained were ω_1 (Na-N stretch)=178.9 cm⁻¹, ω_2 (degenerate bend)=146.1 cm⁻¹, and ω_3 (N-N stretch)=2214.1 cm⁻¹, at the MP2/6-311G(2df) level, with the corresponding values at the MP2/aug-cc-pVTZ level being 183.7, 140.7, and 2197.0 cm⁻¹. These values may be compared to values obtained previously (at the HF level), $\omega_1=167$ cm⁻¹, $\omega_2=142$ cm⁻¹, and $\omega_3=2743$ cm⁻¹ (Ref. 17), and $\omega_1=174$ cm⁻¹, $\omega_2=156$ cm⁻¹, and $\omega_3=2748$ cm⁻¹ (Ref. 6, unscaled). It is noteworthy that the values obtained previously at the HF level, and those obtained here at the MP2 level are very similar.

These harmonic values for the vibrational frequencies will be compared below to the anharmonic vibrational sepa-

TABLE II. Interaction energies and basis set superposition errors calculated at the respective optimized geometries (cm^{-1}). ($1s$ orbital on Na^+ frozen.)

Method	Basis set	BSSE(Na^+)	BSSE(N_2)	BSSE(tot)	ΔE_{CP}
MP2	6-311+G($2df$)	216.5	177.3	393.8	2532.4
MP2	aug-cc-pVQZ	108.4	87.6	196.0	2730.8
CCSD(T)	aug-cc-pVTZ	95.1	210.9	306.0	2711.9
CCSD(T)	aug-cc-pVQZ	109.5	83.0	192.5	2757.1

rations obtained from the fitted potential energy hypersurface, calculated at the CCSD(T)/aug-cc-pVTZ level of theory.

B. Interaction energies

The interaction energies, and associated basis set superposition energies, as calculated at the respective optimized geometries, are presented in Table II, where only the $1s$ orbital on Na^+ was frozen. The corresponding quantities as calculated at the CCSD(T)/aug-cc-pVQZ-optimized geometry are shown in Table III, where all electrons were correlated. As may be seen from the results in Table II, the MP2/6-311G($2df$) interaction energy is significantly lower than that obtained at the higher levels of theory. Interestingly, the MP2 and CCSD(T) results obtained using the aug-cc-pVQZ basis set are very similar to each other, indicating that it is the quality of the basis set that is the more important factor for $\text{Na}^+\cdot\text{N}_2$. The results in Table III indicate that at a geometry calculated at a reasonable level of theory, the interaction energy obtained using different levels of theory is very similar. The most important conclusion from Table III is that at the CCSD(T) level, the values obtained using the aug-cc-pVTZ, aug-cc-pVQZ, and aug-cc-pV5Z level are very similar (the largest difference is 53 cm^{-1} , which is $<2\%$ of the interaction energy). This indicates that a potential energy hypersurface calculated at the CCSD(T)/aug-cc-pVTZ level should be reliable for the calculation of the low-lying energy levels.

Our most reliable value for $\Delta E_e(\text{Na}^+\cdot\text{N}_2)$ is that calculated at the CCSD(T)/aug-cc-pV5Z//CCSD(T)/aug-cc-pVQZ level of theory, 2766.8 cm^{-1} (7.91 kcal^{-1}), a value not too dissimilar to some of the previously reported values. This may not be compared directly to the experimental values, since experiments tend to determine the enthalpy. The binding enthalpy and ΔH_f^{298} for $\text{Na}^+\cdot\text{N}_2$ are calculated below.

TABLE III. Calculated interaction energies (cm^{-1}) at the CCSD(T)/aug-cc-pVQZ-optimized geometry. (All electrons correlated.)

Method	Basis set		BSSE(Na^+)	BSSE(N_2)	BSSE(tot)	ΔE_{CP}
	aug-cc-pVXZ					
MP2	T		109.9	200.8	310.7	2696.0
	Q		166.5	88.5	255.0	2738.6
	5		194.4	52.7	247.1	2749.6
CCSD	T		108.1	207.0	315.1	2670.4
	Q		166.0	79.6	245.6	2711.0
	5		192.4	46.2	238.6	2719.7
CCSD(T)	T		110.6	210.9	321.5	2713.5
	Q		168.1	83.0	251.1	2756.9
	5		195.1	77.5	242.6	2766.8

Note that the BSSE is $<9\%$ of the interaction energy, which is acceptable. As the basis set size increases, the total BSSE decreases, as expected, but note that for Na^+ , the BSSE increases as the basis set increases—contrary to expectations. This point has been discussed previously.⁴

C. Potential energy surface and anharmonic vibrational levels

The potential energy hypersurface was obtained by fitting a grid of geometries and energies obtained at the CCSD(T)/aug-cc-pVTZ level of theory (BSSE corrected), to a potential energy function of the form,

$$V(R, \alpha) = \sum_i c_i \{1 - \exp[-a_R(R - R_e^F)]\}^{q_i} P_{r_i}(\cos \alpha).$$

This potential energy function has the same form as used to generate potential energy surfaces for $\text{Ar}\cdot\text{NO}^+$ (Refs. 23 and 24). R is the Jacobi bond distance (R_e^F is the fitted equilibrium value), α is the Jacobi bond angle (the angle between \mathbf{R} and the N_2 bond axis), and $P_k(\cos \alpha)$ are the Legendre polynomials. Numerical values of c_i were obtained by fitting $V(R, \alpha)$ to the calculated grid of energy points, which sampled the whole angular space, and a large range of intermolecular distances. The values of c_i obtained are given in Table IV. The potential was then substituted into the well-known, body-fixed Hamiltonian in atom-diatom scattering coordinates.²⁵ The eigenvalue problem was then solved by diagonalizing the Hamiltonian as a matrix over the basis functions, which were expressed as products of the standard (analytic) “free rotor” functions and numerical eigenfunctions of the “pure stretching” Schrödinger equation, characterized by $V(R, \alpha)$. The resulting eigenvalues correspond to the anharmonic vibrational frequencies, and are given in Table V.

These values are expected to be more reliable than the harmonic values obtained above (and, indeed, are at a higher level of theory). Note that the interaction between the intermolecular vibrations and the N–N stretch has been neglected in this treatment; however, given the large magnitude of the latter, relative to the intermolecular ones, this interaction is unlikely to be significant (at least in the low-energy region).

A comparison between the two sets of harmonic and anharmonic 1–0 values indicates that the $\text{Na}^+\cdot\text{N}_2$ intermolecular stretch, σ , is not very anharmonic (best harmonic value is 184 cm^{-1} vs an anharmonic value of 170 cm^{-1}), and neither is the intermolecular bend (best harmonic value is 141 cm^{-1} vs an anharmonic value of $134\text{--}135\text{ cm}^{-1}$; note that this value is half of the bend fundamental calculated from the hypersurface, see Ref. 26). The anharmonicity is

TABLE IV. Fitted potential energy parameters for the Na⁺·N₂ intermolecular potential energy surface.^a

q_i	r_i	c_i
2	0	11587.084
3	0	-27821.755
4	0	30759.944
5	0	-17375.162
6	0	4070.654
0	2	-1447.141
1	2	-1619.063
2	2	18595.188
3	2	-40235.696
4	2	43264.732
5	2	-24406.816
6	2	5837.305
0	4	3.500
1	4	-1075.548
2	4	4875.423
3	4	-9753.809
4	4	10867.100
5	4	-6680.044
6	4	1761.956
0	6	16.353
1	6	-153.623
2	6	603.325
3	6	-1163.745
4	6	1057.862
5	6	-357.872
0	8	1.402
1	8	-11.789
2	8	25.199
3	8	-15.476

^a $a_R = 0.51 \text{ \AA}^{-1}$, R_e^F (Jacobi) = 2.926 358 \AA ; see text for details.

thus rather small near the bottom of the potential well, which is not so surprising, given that the binding energy is $>2700 \text{ cm}^{-1}$. If, however, one looks at a series of the intermolecular stretch, then successive separations of 169, 163, 155, 141, 134, 128, and 99 cm^{-1} are obtained; for the intermolecular bend, the separations are 134, 130, 124, 119, and 112 cm^{-1} . These values indicate that anharmonicity plays a much greater role further up the potential well, as expected. The conclusion is that anharmonicity is relatively unimportant if the complex only has the lowest few vibrational levels populated (as might be expected if it is formed from low-energy collisions/reactions), but may well be important if the complex is formed from either high-energy collisions, or via photoionization.

Note that, from the fitted form of $V(R, \alpha)$ it is possible to determine the position of the minimum of the hypersurface. The minimum of $V(R, \alpha)$ was calculated to be at $R_{\text{Na-N}} = 2.4710 \text{ \AA}$, which compares to the optimized value for R of 2.4460 \AA at the CCSD(T)/aug-cc-pVTZ level of theory (see Table I). The small difference in these two values is due to the point-by-point (*a priori*) correction for BSSE in the calculation of the hypersurface, but a single-point correction of the interaction energy at the calculated minimum (*a posteriori*), and the error in the fitting itself. $D_e (= \Delta E_e)$ is derived as 2699 cm^{-1} from the fitted hypersurface, which compares well to the D_e value of 2712 cm^{-1} (Table II). Also from the fitted hypersurface, it was possible to calculate the position of the T-shaped saddle point, which was found to be

TABLE V. Anharmonic vibrational frequencies (cm^{-1}) calculated as the eigenvalues of the Sutcliffe–Tennyson Hamiltonian, with the potential energy function given by $V(R, \alpha)$, see text.

State		Energy ^a		
v_b	v_s	Adiabatic	Variational	Perturbative ^b
0	0	0.0	0.0	0.0
0	1	169.9	169.5	169.5
0	2	332.3	331.8	331.8
0	3	487.4	486.9	486.9
0	4	635.3	634.8	634.7
0	5	776.1	775.6	775.6
0	6	910.0	909.8	909.8
0	7	1036.8	1038.0	1038.1
0	8	1156.6	1143.4	1144.0
0	9	1269.4	1261.0	{1264}
0	10	1375.3	1360.0	1360.2
2	0	529.8	527.2	527.7
2	1	691.9	683.6	684.0
2	2	846.9	834.1	834.5
2	3	994.7	978.2	978.5
2	4	1135.3	1114.9	1115.1
2	5	1268.5	1243.4	{1246}
4	0	1020.2	1012.8	1013.7
4	1	1175.5	1153.0	1153.6
4	2	1323.1	1289.9	1289.9
1	0	269.3	268.4	268.6
1	1	435.1	431.9	432.1
1	2	593.6	588.8	589.0
1	3	745.1	738.9	739.1
1	4	889.7	881.8	882.0
1	5	1027.4	1017.2	1017.4
1	6	1157.9	1162.1	1162.1
1	7	1281.2	1283.4	1283.8
3	0	780.5	775.6	776.3
3	1	939.2	924.1	924.7
3	2	1090.5	1067.7	1068.2
3	3	1234.4	1205.4	1206.4
3	4	1370.6	1335.7	1336.7
5	0	1247.7	1237.7	1238.6
5	1	1399.5	1369.4	1371.8

^aEnergies are given relative to the zero-point level. Vibrational energy levels with $v_b \neq 0$ include contributions from both of the degenerate π bending vibrations.

^bValues given in braces are obtained by interpolation, see Ref. 27.

at $R_{\text{Na-N}} = 2.8886 \text{ \AA}$, and at an energy of 2198 cm^{-1} above the bottom of the well.

D. Rovibrational energy levels

Table VI gives a selection of the calculated rotational energy levels for the lowest vibrational states of Na⁺·N₂. These are calculated by diagonalizing the Sutcliffe–Tennyson Hamiltonian²⁵ but discarding the off-diagonal Coriolis terms. The diagonalization was performed both variationally, and perturbatively with the perturbation treatment having been described previously in Ref. 27. The perturbation approach yields zeroth-order energies, and corrections, explicitly in terms of the pertinent quantum numbers, and thus give (unlike the variational calculation) direct assignment of the calculated states. Often, only the adiabatic approach is employed; however, here this is used as the zeroth order approximation in the perturbation treatment. The variational treatment is more numerically robust; however, it does

TABLE VI. Rovibrational levels (cm^{-1}) for the lowest vibrational states of $\text{Na}^+\cdot\text{N}_2$.

J	K	(v_s, v_b)							
		(0,0)	(1,0)	(0,1)	(2,0)	(1,1)	(3,0)	(0,2)	(1,2)
0	0	0.000	(169.538) ^a	(268.363) ^a	(331.822) ^a	(431.858) ^a	(486.868) ^a	(527.178) ^a	(588.778) ^a
1	0	0.291	0.284	0.292	0.278	0.242	0.272	0.294	0.281
2	0	0.872	0.854	0.877	0.835	0.860	0.816	0.882	0.841
5	0	4.360	4.269	4.388	4.176	4.299	4.082	4.411	4.205
10	0	15.984	15.651	16.087	15.310	15.759	14.964	16.172	15.413
1	1	136.367	133.669	131.711	131.320	128.420	129.242	126.678	125.470
2	1	136.950	134.240	132.298	131.880	128.995	129.789	127.268	126.033
5	1	140.451	137.669	135.820	135.234	132.445	133.067	130.805	129.407
10	1	152.117	149.093	147.553	146.410	143.940	143.990	142.593	140.648
2	2	272.268	266.873	262.835	262.150	256.305	257.928	252.621	250.458
5	2	275.781	270.315	266.367	265.517	259.766	261.219	256.167	253.843
10	2	287.489	281.783	278.135	276.736	271.299	272.182	267.983	265.120

^aNote that the subsequent energy levels given in the respective columns, are relative to the pure vibrational energy levels.

not give a direct assignment of the quantum numbers of the calculated levels, as does the perturbation treatment. As may be seen from Table V, all three approaches give similar energies, but the variational ones are expected to be the most reliable, with the assignments coming from the perturbational calculations.

Note that because $\text{Na}^+\cdot\text{N}_2$ is linear, then the bending levels contribute angular momentum along the internuclear axis, and consequently, in principal it is necessary to specify the *e/o* parity, as well as the standard *J* and *K* quantum numbers, which are appropriate for the bent form of the complex. As it turns out, the barrier to internal rotation is too high for the parity splittings for the low energy levels of interest here to be determined. Discussion on these quantum numbers and specifically the correlation between energy labels of linear and bent forms of quasilinear molecules has been presented previously.^{26,28}

The rotational levels in Table VI should prove useful for characterization of $\text{Na}^+\cdot\text{N}_2$, either via microwave spectroscopy, or high-resolution photoelectron spectroscopy.

E. Binding enthalpy and enthalpy of formation

The enthalpy of formation was calculated within the RRHO approximation for the linear equilibrium geometry. In this case, the rotational contribution to the enthalpy for $\text{Na}^+\cdot\text{N}_2$ was just taken as the classical RT term. The vibrational contribution was calculated by employing the harmonic vibrational frequencies obtained at the MP2/aug-cc-pVTZ level. As discussed in the previous subsection, the effects of anharmonicity are quite small in the present case. In addition, the intermolecular vibrational frequencies have a significant magnitude, and consequently, their impact on the vibrational partition function is quite small. Thus, the use of the harmonic oscillator approximation here is not expected to lead to a significant error. Regarding the rigid rotor approximation, whether this is a good approximation or not depends on the ‘‘floppiness’’ of the molecule. As noted above, the position of the T-shaped transition state was found to be significantly above the minimum energy structure and in addition the binding energy of the linear structure is $>2700\text{ cm}^{-1}$; consequently, we conclude that any effects of

internal rotation, or floppiness, are going to be small (kT at $298\text{ K} \sim 200\text{ cm}^{-1}$). In addition, in the upper atmosphere, where $\text{Na}^+\cdot\text{N}_2$ plays its role in the sporadic sodium layer formation, only the lowest internal energy levels are expected to contribute, so again, the calculated enthalpies are not expected to be affected greatly by the simplified approaches used here.

Table VII contains the calculated enthalpy change for two reactions. These two reactions were chosen as $\text{Na}^+\cdot\text{N}_2 \rightarrow \text{Na}^+ + \text{N}_2$, which is simply the dissociation of the complex (and so yields the binding enthalpy); and $\text{Na}^+\cdot\text{N}_2 + \text{O} \rightarrow \text{NaO}^+ + \text{N}_2$, which has been noted by Cox and Plane⁷ as being one of the key reactions in the Na^+ reaction scheme for the formation of the sporadic sodium layers. Using well-established values for the enthalpies of formation of the other species involved, $\Delta H_f^{298}(\text{Na}^+\cdot\text{N}_2)$ may be derived as $136.5 \pm 2.0\text{ kcal mol}^{-1}$, where the error has been selected to cover the two calculated values, to encompass the expected inaccuracies in the simplified approach used, and to cover the inaccuracies in the ΔH_f^{298} values of the other species. The standard ΔH_f^{298} values were taken as 0 kcal mol^{-1} for N_2 (by definition); $144.1\text{ kcal mol}^{-1}$ for Na^+ (Ref. 29); $59.56\text{ kcal mol}^{-1}$ for O (Ref. 29); and $196.5 \pm 1.5\text{ kcal mol}^{-1}$ for NaO^+ (Ref. 1). (Note that the stationary electron convention is used.)

It is clear from the values in Table VII that the two reactions used lead to very similar values of $\Delta H_f^{298}(\text{Na}^+\cdot\text{N}_2)$. Thus, we are confident that the quoted value is close to the true one. The calculated ΔE_e for the

TABLE VII. Calculated energy changes (ΔE_e), CP corrected, and the enthalpy correction terms (ΔE^{them}) using the RRHO approximation (kcal mol^{-1}).

Method	$\text{Na}^+\cdot\text{N}_2 \rightarrow \text{Na}^+ + \text{N}_2$	$\text{Na}^+\cdot\text{N}_2 + \text{O} \rightarrow \text{NaO}^+ + \text{N}_2$
CCSD/aug-cc-pVQZ	7.751	1.194
CCSD(T)/aug-cc-pVQZ	7.882	1.253
CCSD/aug-cc-pV5Z	7.776	1.206
CCSD(T)/aug-cc-pV5Z	7.911	1.261
ΔE^{them}	-0.381	-0.498
$\Delta H_f^{298}(\text{Na}^+\cdot\text{N}_2)$	136.6	136.2

reactions indicate that the levels of theory used are satisfactory, with the basis set effect being close to saturation, and the effect of higher-order excitations (triples) being rather small: these two effects are well within the error range quoted. The binding enthalpy obtained is 7.7 kcal mol⁻¹, which compares extremely favorably with the experimental value of 8 kcal mol⁻¹ (Ref. 15), and the previous *ab initio* value of 7.43 kcal mol⁻¹ (Ref. 17).

IV. CONCLUSIONS

The equilibrium geometry and interaction energy of the Na⁺·N₂ complex have been calculated at high levels of theory. The complex has a linear equilibrium geometry, with a Na⁺·N bond length of 2.446 Å, and a N–N bond length of 1.097 Å. The most reliable value of the interaction energy, ΔE_e , is calculated to be 2770 cm⁻¹.

A large grid of potential energy points has been calculated at the CCSD(T)/aug-cc-pVTZ level of theory and fitted to an analytic function, from which anharmonic vibrational separations, as well as rotational energy levels have been calculated. It was found that for vibrational energy levels close to the potential minimum, anharmonicity was quite small. The energy levels presented herein, together with the potential energy hypersurface should prove useful to experimental characterization of the Na⁺·N₂ molecular complex, as well as to an understanding of Na⁺/N₂ collisions, and so Na⁺·N₂ formation in the atmosphere.

The binding enthalpy is calculated as 7.7 kcal mol⁻¹, and $\Delta H_f^{298}(\text{Na}^+\cdot\text{N}_2)$ is calculated as 136.5 ± 2.0 kcal mol⁻¹.

ACKNOWLEDGMENTS

The authors are grateful to the EPSRC for the award of computer time at the Rutherford Appleton Laboratories, which enabled these calculations to be performed. P.S. is grateful to the Royal Society and NATO for the award of a postdoctoral fellowship. E.P.F.L. is grateful to the Research Committee of the Hong Kong Polytechnic University and the Research Grant Council of the HKSAR for support. T.G.W. is grateful to the EPSRC for the award of an Advanced Fellowship. V.S. is grateful to the Grant Agency of the Academy of Sciences of the Czech Republic (Grant No. A4040806) for support.

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