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The intermolecular potential energy surface of the He·NO$^+$ cationic complex

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Close-coupling calculations of bound rotational and vibrational states are carried out on a new intermolecular potential energy function based on 200 energies of the He·NO$^+$ cationic complex calculated at the coupled-cluster single double (triple)/aug-cc-pV5Z *ab initio* level of theory at a range of geometries and point-by-point corrected for basis set superposition error. The potential energy function is constructed by combining the reciprocal power reproducing kernel Hilbert space interpolation with Gauss–Legendre quadrature. The best estimate of the intermolecular dissociation energy, D_e, is 198±4 cm^{-1}, obtained by extrapolations to the complete basis set limit, and calculating estimates for relativistic effects and core and core-valence correlation effects. *© 2002 American Institute of Physics.* [DOI: 10.1063/1.1433507]

I. INTRODUCTION

The interaction between a rare gas atom and a closed-shell diatom represents one of the simplest atom–molecule interactions. Such interactions are, however, difficult to study as the surfaces are very shallow, and zero-point energies often form a large percentage of the total binding energy, leading to very floppy systems. On the other hand, complexes between a rare gas atom and a closed-shell cation are much more strongly bound. In addition, such species are a good test of the accuracy and reliability of modern *ab initio* methods, as the whole potential energy surface (PES) may be calculated with modern codes and computers. Such PESs may be employed to calculate spectroscopic quantities, which may be compared to experiment, where available, and the reliability of the methodology judged. Such surfaces are of use in the calculation of transport properties[1] and collisional dynamics.[2–4] The interaction between NO$^+$ and He is also inevitably important in the detailed understanding of NO$^+$ embedded in helium droplets: Callicoatt *et al.*[5] have shown that He$^+$ charge transfers to NO with a very high probability in such an environment. In addition, the work is also pertinent to Rydberg states of NO interacting with rare gas matrices and liquid rare gases.[6]

There have been several theoretical studies of the He·NO$^+$ species. Robbe *et al.*[7] performed a CIPSI set of calculations using a relatively small basis set, generating a PES for He·NO$^+$. They deduced a single energy minimum at $R = 2.96$ Å and $\theta = 109.9°$, where R and θ are Jacobi coordinates, defined in Sec. II. Zenevich *et al.*[2] generated a global PES based on the Gislason–Ferguson model,[8] but with a number of assumptions about various parameters. The most detailed surface prior to the present study was that from Pogrebnya *et al.*[3] Their surface was based on 210 points calculated at the CCSD(T) *ab initio* level of theory. The basis set consisted of the *sp* functions from the standard aug-cc-pVQZ basis set, combined with the *d* and *f* functions from the standard aug-cc-pVTZ basis set for N and O, with the He basis set being $(8s3p2d)/[4s3p2d]$. By comparing the calculated dissociation energy employing this basis set with that calculated using aug-cc-pVQZ (no g) and the full aug-cc-pVQZ basis sets, it was concluded that the resulting surface should be very accurate. The dissociation energy was calculated to be $D_e \approx 186.5$ cm^{-1}, the minimum energy geometry being $R = 2.80$ Å and $\theta = 79.8°$. Finally, Viehland and co-workers[1] recently calculated a surface at the MP4(SDTQ)/6-311+G(2*df*,*p*) level of theory, obtaining a minimum energy geometry of $R = 2.90$ Å and $\theta = 80°$. We note that recently we calculated the dissociation energy of He·NO$^+$ using a variety of basis sets from aug-cc-pVDZ through to aug-cc-pV5Z employing MP2, MP4, QCISD(T), and CCSD(T) methods. In that work, our best value for dissociation energy of He·NO$^+$ was $D_e = 192.1$ cm^{-1} obtained at the CCSD(T)/aug-cc-pV5Z//QCISD/aug-cc-pVTZ level of theory.[9]

The present work also follows on from that of Ar·NO$^+$, whose PES has been investigated by Wright and co-workers in some detail.[10–12] In that work, it was found that the MP2

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[b)] Electronic mail: epl@soton.ac.uk

[c)] Electronic mail: T.G.Wright@sussex.ac.uk method performed to a very high level of accuracy with regard to the vibrational frequencies, although it was clear that this was due to a fortuitous cancellation of errors. The $\mathrm{He} \cdot \mathrm{NO}^+$ complex is more weakly bound than $\mathrm{Ar} \cdot \mathrm{NO}^+$, owing to the lower polarizability of He compared to Ar. Consequently the basis set superposition error is likely to be, percentagewise, more important, and therefore using a rather large basis set and performing a full counterpoise correction[13] at each point is necessary. In addition, the highest available level of theory should be used in order to minimize the effects of various approximations on the values of interaction energy.

II. CALCULATIONAL DETAILS

A. *Ab initio* calculations

As the quality of an *ab initio* interaction potential depends greatly on the computational method and basis set employed, our aim is to generate the $\mathrm{He} \cdot \mathrm{NO}^+$ potential energy surface at the highest affordable level of theory. In the present work, we have used a closed-shell variant of the coupled-cluster method[14] with direct single and double excitations and a perturbative treatment of triples [CCSD(T)]. An augmented correlation-consistent polarized valence quintuple-zeta basis set[15] (aug-cc-pV5Z) has been used in its contracted form for He, N, and O. The resulting basis set consists of 334 contracted Gaussian-type orbitals (GTOs) including higher angular momentum and diffuse basis functions. There are 80 GTOs on He $[6s5p4d3f2g]$ and 127 GTOs $[7s6p5d4f3g2h]$ on both N and O. Only valence orbitals were correlated in the calculations, i.e., orbitals 1*s* on O and 1*s* on N were kept frozen in the coupled-cluster calculations.

Jacobi coordinates R, θ, and r were used to parametrize the molecule. R is the distance of He to the center of mass (c.m.) of NO^+, θ corresponds to the angle He–c.m.–N, and r is the NO^+ bond length. The NO^+ bond length r was kept fixed at its experimental equilibrium value,[16] $r_e = 1.063\,22$ Å. Interaction and vibrational energies are reported with respect to the $\mathrm{He}+\mathrm{NO}^+$ dissociation limit.

The intermolecular potential, $\mathcal{V}(R,\theta)$, is defined as the electronic energy, $\mathcal{W}(R,\theta)$, of the complex with respect to that of the monomers. In practice, it is important to include the counterpoise correction[13] for the basis set superposition error, so that the monomer energies are calculated in the complete supermolecular basis set (and therefore dependent on R and θ)

$$\mathcal{V}(R,\theta)=\mathcal{W}_{\mathrm{HeNO}^+}(R,\theta)-\mathcal{W}_{\mathrm{He}}(R,\theta)-\mathcal{W}_{\mathrm{NO}^+}(R,\theta). \tag{1}$$

The comparison of monomer energies $\mathcal{W}_{\mathrm{He}}$ and $\mathcal{W}_{\mathrm{NO}^+}$ with those calculated in the monomer basis set alone shows that the total basis set superposition error is not larger than 3 cm^{-1} in the region of the potential well. This indicates that basis set superposition error is almost converged with respect to the basis set. The counterpoise-corrected interaction energies $\mathcal{V}(R_i,\theta_j)$ were calculated for 200 points on the product grid (R_i,θ_j), where $R_i = 1.0$, 1.3,1.5, 1.65, 1.8, 2.0, 2.2, 2.4, 2.6, 2.7, 2.8, 2.9, 3.0, 3.2, 3.5, 4.0, 5.0, 7.0, 10.0, 15.0 and θ_j, $j=1,\ldots,10$, were selected so that $\cos\theta_j$ are the zeros of the Legendre polynomial $P_{10}(x)$. All *ab initio* calculations were carried out using the MOLPRO 2000.1 program suite.[17,18]

B. Potential energy surface

The potential energy function $V(R,\theta)$ used for the bound-state calculations was represented in terms of radial functions $V_\lambda(R)$ and Legendre polynomials $P_\lambda(\cos\theta)$

$$V(R,\theta)=\sum_{\lambda=0}^{9} V_\lambda(R)\, P_\lambda(\cos\theta). \tag{2}$$

The radial functions were constructed from the *ab initio* points, $\mathcal{V}(R_i,\theta_j)$, by combining the reciprocal power reproducing kernel Hilbert space interpolation procedure (RP-RKHS)[19,20] with Gauss–Legendre quadrature

$$V_\lambda(R)=\sum_{i=1}^{20} \alpha_{i\lambda}^{[n,m]}\, q^{[n,m]}(R^l,R_i^l), \tag{3}$$

where

$$\alpha_{i\lambda}^{[n,m]}=\frac{2\lambda-1}{2}\sum_{j=1}^{10} w_j\, \alpha_i^{[n,m]}(\theta_j)\, P_\lambda(\cos\theta_j) \tag{4}$$

and w_j are Gauss-Legendre weights corresponding to abscissas $\cos\theta_j$, $j=1,\ldots,10$. For each j the coefficients $\alpha_i^{[n,m]}(\theta_j)$ are solutions of the system of linear equations

$$\mathcal{V}(R_k,\theta_j)=\sum_{i=1}^{20} \alpha_i^{[n,m]}(\theta_j)\, q^{[n,m]}(R_k^l,R_i^l),$$
$$k=1,2,\ldots,20. \tag{5}$$

In order to obtain the correct long-range behavior[21] of the interaction potential

$$\mathcal{V}(R,\theta)\sim-\frac{C_4}{R^4}-\frac{C_6(\theta)}{R^6}+\cdots, \tag{6}$$

we choose $l=2$ and the RP-RKHS parameters as $m=1$ and $n=2$, i.e.,

$$q^{[2,1]}(x,y)=\frac{2}{3z_>^2}\left(1-\frac{1}{2}\frac{z_<}{z_>}\right), \tag{7}$$

where $z_< = \min(x,y)$ and $z_> = \max(x,y)$. This choice also ensures that the radial functions $V_\lambda(R)$, as well as their first and second derivatives, are continuous.

C. Bound states

The nuclear Schrödinger equation is solved for bound states of $\mathrm{He} \cdot \mathrm{NO}^+$ in the atom plus rigid-rotor approximation, where states can be characterized by the energy E, the total angular momentum J, its body fixed projection K, and the parity label e or f.[22] Levels with $K=0$ have parity e while states with $|K|>0$ are split by the Coriolis coupling into pairs with e and f parity. The total wave function is expanded using a basis set of NO^+ rotational wave functions for the four angular coordinates (the potential anisotropy mixes the NO^+ rotational levels, so the NO^+ rotational quantum number j is no longer a good quantum number). The Schrödinger equation, projected on this basis set for each total angular

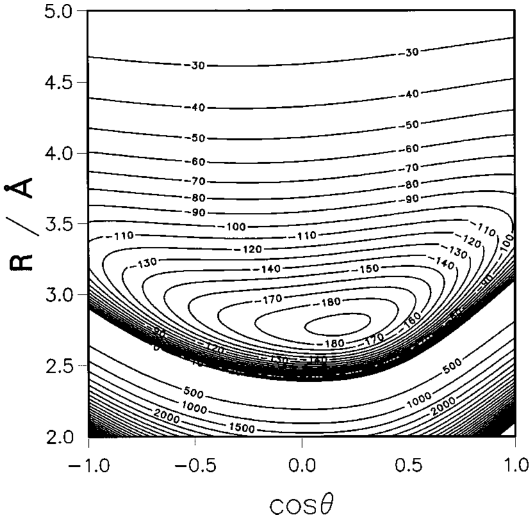

FIG. 1. Contour plot of the potential energy surface of He·NO$^+$.

momentum J and parity, is written as a set of coupled differential equations in R. The close-coupled equations were solved using the diabatic modified log-derivative method,[23] for step sizes $h=0.005$ and 0.01 Å with a grid from 1.6 to 30.0 Å. The results were extrapolated to zero step size using the Richardson h^4 extrapolation.[24] The resulting eigenvalues are converged to better than 0.001 cm^{-1}. The actual bound-state calculations were carried out using the BOUND program.[24,25]

III. RESULTS AND DISCUSSION

A. Equilibrium geometry and the potential energy surface

The contour plot of the resulting intermolecular potential energy surface is shown in Fig. 1. It has a single minimum at $R_e=2.782$ Å, $\theta_e=79.34°$ at an energy of 193.2 cm^{-1} with respect to the He+NO$^+$ asymptote. These values are compared to previous *ab initio* calculations[1–3,7,9] in Table I.

As in the case of the Ar·NO$^+$ cationic complex,[10–12] our surface differs significantly from that of Robbe *et al.*[7] Contrary to Ref. 7 our results indicate that He is lying on the nitrogen side of the molecule. Viehland *et al.*[1] used the NO$^+$ bond length fixed at the value obtained from an HF/6-311+G(2*df,p*) geometry optimization, and this value differs significantly from the experimental NO$^+$ bond length. Although they did not correct the potential energies for the basis set superposition error, their minimum energy geometry agrees reasonably well with ours. It is clear from the values in Table I that the results from Ref. 3 are extremely close to the values obtained herein.

TABLE I. Equilibrium geometry and dissociation energy of He·NO$^+$.

Authors	R_e (Å)	θ_e (°)	r_e (Å)	D_e (cm^{-1})
Robbe *et al.*[a]	2.96	109.9	1.063 2	248
Pogrebnya *et al.*[b]	2.80	79.8	1.063 2	186.4
Viehland *et al.*[c]	2.9	80.0	1.026 2	146
Lee *et al.*[d]	2.79	84.3	1.063	192.1
This work[e]	2.782	79.34	1.063 22	193.2

[a] r_e fixed; Ref. 7.

[b] r_e fixed; Ref. 3.

[c] r_e fixed; Ref. 1.

[d] Full 3D optimization at the QCISD/aug-cc-pVTZ level of theory; D_e calculated and counterpoise-corrected at the CCSD(T)/aug-cc-pV5Z level of theory; Ref. 9.

[e] r_e fixed at the experimental value.

TABLE II. Calculated intermolecular vibrational levels (cm^{-1}) of He·NO$^+$ (ν_σ denotes the intermolecular stretch and ν_β denotes the intermolecular bend; the assignment of the higher energy levels is tentative).

ν_σ	ν_β	Adiabatic[a]	Nonadiabatic[b]
0	0	−131.535	−129.353
0	1	−106.759	−102.940
0	2	−83.926	−84.464
1	0	−68.580	−70.079
0	3	−62.147	−58.298
1	1	−51.184	−53.245
0	4	−39.174	−38.560
1	2	−33.555	−33.713
2	0	−28.801	−27.974
2	1	−17.822	−17.399
1	3	−13.779	−15.554
0	5	−13.329	−13.764
3	0	−9.119	−7.268
2	2	−4.590	−3.561
3	1	−2.268	−1.786
4	0	−1.869	−0.218

[a] Adiabatic approximation calculation.

[b] Close-coupling calculation.

For the present surface, linear saddle points are located at $R=3.487$ Å for He–NO$^+$ and at $R=3.277$ Å for He–ON$^+$, 98.7 and 112.7 cm^{-1} below the dissociation threshold respectively.

B. Rovibrational states

Vibrational energy levels are presented in Table II. In order to get an approximate assignment we also performed calculations in the adiabatic approximation. The assignment is given in terms of the stretch, ν_σ, and bend, ν_β, quantum numbers, and is presented together with the corresponding adiabatic energies in Table III. At low energies, this assignment is probably quite reasonable; however, to higher energy, the coupling of the bend and stretch vibrations will eventually render an assignment in terms of these quantum numbers meaningless. These energies should prove useful in the assignment of either infrared spectra of He·NO$^+$ or ZEKE photoelectron spectra of He·NO.

The results of rotational energy calculations are shown in Table III for the ground vibrational state. At low J, the assignment should be relatively reliable and these values should prove useful in the assignment of microwave or rotationally resolved infrared spectra of He·NO$^+$. However, at high J the rotational energy spacing will become comparable to the vibrational energy spacing, and almost free internal rotation of NO$^+$ will occur, making assignment of rotational levels difficult.

TABLE III. Calculated rotational energies (cm^{-1}) of the ground vibrational state $(\nu_\sigma=0,\nu_\beta=0)$.

J	K	p	$E(J,K,p)$	J	K	p	$E(J,K,p)$
0	0	*e*	0.000	3	1	*f*	8.204
1	0	*e*	1.008	3	2	*e*	12.907
1	1	*e*	2.694	3	2	*f*	12.875
1	1	*f*	2.849	3	3	e	21.473
2	0	*e*	3.014	3	3	*f*	21.474
2	1	*e*	4.531	4	0	e	9.926
2	1	*f*	4.995	4	1	*e*	10.941
2	2	*e*	9.987	4	1	*f*	12.463
2	2	*f*	9.980	5	0	*e*	14.759
3	0	*e*	5.998	5	1	*e*	15.500
3	1	*e*	7.281	5	1	*f*	17.755

C. Dissociation energy

As may be seen from Table I, the value for the dissociation energy from Robbe *et al.*[7] is far too high: since it is clear from the fact that their minimum energy geometry is in disagreement with that obtained by ourselves and those from Refs. 1 and 3, we conclude that there is something fundamentally wrong with that PES and discuss it no further.

The binding energy is severely underestimated in Ref. 1 when compared to our value of 193.2 cm^{-1}. Moreover, as mentioned previously, no counterpoise correction for basis set superposion error was made by Viehland *et al.*,[1] and this would make the dissociation energy even lower. The basis set they used is rather small, and we have previously shown[9] that the basis set is the main factor in calculating the dissociation energies of the $\mathrm{Rg\cdot NO^+}$ cationic complexes at a correlated *ab initio* level.

On the other hand, the value from Ref. 3 is in a good agreement with our value; however, it is clear that the basis set limit has not yet been reached in either study. For this reason we perform further calculations and use extrapolation techniques to obtain a better estimate of the dissociation energy (see the following).

At the minimum energy geometry of the potential energy surface additional single-point CCSD(T) calculations were performed using s-aug-cc-pVXZ, X=T,Q,6, and d-aug-cc-pVXZ, X=T,Q,5, where s-aug-cc-pVXZ (s implies singly augmented) is actually the standard aug-cc-pVXZ basis set, and d-aug-cc-pVXZ is the aug-cc-pVXZ basis set augmented in the even-tempered manner by additional set of diffuse functions (d implying doubly augmented). The results of these additional single-point calculations are summarized in Table IV (all interaction energies were counterpoise corrected for the basis set superposition error). As may be seen, the results obtained using the d-aug-cc-pVXZ basis sets converge slightly faster than those obtained using the s-aug-cc-pVXZ ones. As the quality of basis sets is improved with increasing X, the most reliable estimate of the interaction energy in the complete basis set limit, $\Delta E(R_e,\theta_e;\infty)$, should be obtained by extrapolating energies corresponding to the highest X values. Applying the two-point extrapolation formula

$$\Delta E(R_e,\theta_e;\mathrm{X})=\Delta E(R_e,\theta_e;\infty)+A(R_e,\theta_e)\,\mathrm{X}^{-3} \qquad (8)$$

by Helgaker *et al.*[26,27] to the aug-cc-pVXZ, X=5,6, interaction energies we obtain 198.7 cm^{-1}. The same formula applied to d-aug-cc-pVXZ, X=Q,5, gives 198.1 cm^{-1}. However, these values are still subject to errors that arise from relativistic, and core and core-valence correlation effects.

TABLE IV. CCSD(T) intermolecular interaction energies (cm^{-1}) calculated at the CCSD(T)/aug-cc-pV5Z counterpoise-corrected minimum using s-aug-cc-pVXZ and d-aug-cc-pVXZ basis sets.

X	s-aug-cc-pVXZ	d-aug-cc-pVXZ
T	181.4	185.0
Q	189.1	193.3
5	193.2	195.6
6	195.5	

An estimate of the relativistic corrections to the interaction energy were made by computing the expectation values of the mass-velocity and one-electron Darwin integrals within the Cowan–Griffin approach[28] at the Hartree–Fock level. The correction was found to be negligible (≈ 0.04 cm^{-1}).

An all-electron-correlated calculation with augmented correlation-consistent polarized core-valence quadruple-zeta basis set, aug-cc-pCVQZ,[29] compared to frozen-core aug-cc-pVQZ calculation indicated that the interaction energy would decrease by about 3.5 cm^{-1} owing to the core and core-valence correlation effects. Overall, then, we cite a final value of $\Delta E(R_e,\theta_e;\infty)=198\pm 4\ \mathrm{cm}^{-1}$. Because the level of theory used to generate the $\mathrm{He\cdot NO^+}$ potential energy surface is very high, we believe that the position of the $\mathrm{He\cdot NO^+}$ minimum is well determined. Therefore we will use the value of $\Delta E(R_e,\theta_e;\infty)$ as an estimate of the $\mathrm{He\cdot NO^+}$ intermolecular dissociation energy $D_e=198\pm 4\ \mathrm{cm}^{-1}$.

IV. CONCLUSIONS

The $\mathrm{He\cdot NO^+}$ cationic complex has been investigated using high level *ab initio* methods. A high-quality potential energy function was constructed from 200 energies calculated at the CCSD(T)/aug-cc-pV5Z level of theory and counterpoise corrected for the basis set superposition error. Vibrational energy levels supported by this potential energy surface, and rotational energy levels of the ground vibrational state were determined by close-coupling calculations. In addition, the intermolecular dissociation energy was calculated using a range of correlation-consistent basis sets and extrapolated to the complete basis set limit. By calculating estimates of the relativistic, and core and core-valence correlation corrections, we obtain a final value of $D_e = 198 \pm 4$ cm^{-1}.

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