# Geometries and Binding Energies of Rg·NO$^+$ Cationic Complexes (Rg = He, Ne, Ar, Kr, and Xe)

**Edmond P. F. Lee**[†]

*Department of Chemistry, University of Southampton, Highfield, Southampton, U.K. SO17 1BJ and Department of Applied Biology and Chemical Technology, Hong Kong Polytechnic University, Hung Hom, Hong Kong*

**Pavel Soldán**[‡]

*Department of Chemistry, University of Southampton, Highfield, Southampton, U.K. SO17 1BJ and*
*J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, 182 23 Prague 8,*
*Doleškova 3, Czech Republic*

**Timothy G. Wright**[§,*]

*Department of Chemistry, University of Southampton, Highfield, Southampton, U.K. SO17 1BJ*

*Received: March 31, 1998; In Final Form: June 15, 1998*

The equilibrium geometries, harmonic vibrational frequencies, and interaction energies of the Rg·NO$^+$ (Rg = He, Ne, Ar, Kr, and Xe) cationic complexes are calculated using a variety of all-electron basis sets and effective core potentials augmented by polarization functions. Calculations are performed at the MP2, QCISD, QCISD(T), CCSD, and CCSD(T) levels of theory for Rg = He and Ne using the all-electron aug-cc-pVXZ [X = D, T, Q, and 5 (for He only)] basis sets; and at the MP2 and QCISD(T) levels for Rg = Ar, Kr, and Xe, using mainly effective core potentials, augmented with polarized valence basis sets. For Ar the results are compared with previous all-electron calculations, to confirm that the basis sets used are adequate. The results indicate that all the complexes are of a skewed T-shaped structure, with the Rg atom on the nitrogen side of the molecule; the Rg—N−O bond angle increases with mass. The interaction energies range from 195 cm$^{-1}$ for He·NO$^+$ to 1980 cm$^{-1}$ for Xe·NO$^+$, in line with expectations based on the increasing polarizability of the Rg atom.

## I. Introduction

The Ar·NO$^+$ cation has received considerable theoretical interest recently, stimulated by the report of the high-resolution zero-kinetic-energy (ZEKE) spectrum by Takahashi.[1] The first calculation was performed by Robbe et al.,[2] who considered not only the Ar·NO$^+$ cation, but also He·NO$^+$. For both cationic complexes it was found that the Rg atom was on the oxygen side of NO$^+$. The method employed was based on a modified CIPSI approach, which uses a size-consistent selection of configurations and second-order Møller−Plesset perturbation theory (this approach is used, because truncated CI calculations are not generally size consistent). Wright et al. in a second study on Ar·NO$^+$ employed MP2 calculations using rather large basis sets (significantly larger than those in ref 2).[3] It was found that the Ar atom was on the nitrogen side of the molecule for all basis sets used. Both of these studies produced potential energy surfaces, which clearly had very different angular dependencies. Because it was not possible to decide definitively which set of calculations was the better, Fourré and Raoult[4] produced two vibrational assignments for the ZEKE spectrum, which differed mainly in the bending levels; in addition, they also noted that they thought that the calculated equilibrium geometry of ref 2 was the more reliable. Wright[5] then followed up the calculations of ref 3 with a set of higher level calculations, up to the QCISD(T)/cc-pVTZ level. In all cases, the calculated geometry indicated that the Ar atom was on the nitrogen side of the complex. In addition, density functional theory (DFT) was used, but although these calculations also indicated that the Ar atom was on the nitrogen side of the molecule, they appeared to over emphasize the intermolecular bonding, as evinced by short bond lengths and high harmonic frequencies.

The aim of the present work was 3-fold: (i) to recalculate the geometry of the He·NO$^+$ cationic complex to see if the He lies on the O or N side of the molecule; (ii) to calculate the equilibrium geometries of Ne·NO$^+$, Kr·NO$^+$, and Xe·NO$^+$; and (iii) to calculate the interaction energies of all of these complexes. In addition, we hoped to establish an economical theoretical methodology from which it would be possible to produce reliable potential energy surfaces.

This work was also stimulated in part by the results from recent resonance-enhanced multiphoton ionization (REMPI) spectroscopic studies, in which an electron is excited on the NO moiety from the $\pi_g$* orbital to a Rydberg orbital. It has been found for the Ar·NO,[6] Kr·NO,[7] and Xe·NO[8] complexes that for the Ã state (corresponding to an electron being excited to the 3s orbital) the core is NO$^+$ and not Rg·NO$^+$, based upon comparisons of observed vibrational spacings and derived dissociation energies with those known or calculated for Ar·NO$^+$. For Kr·NO and Xe·NO, these comparisons cannot be made directly, because no ab initio data yet exists, although

---

[†] E-mail: epl@soton.ac.uk.
[‡] Royal Society Fellow. E-mail: soldan@jh-inst.cas.cz.
[§] E-mail: tgw@soton.ac.uk.

S1089-5639(98)01696-X CCC: $15.00

inferences from the Ar·NO$^+$ data were made. Similar conclusions have also been reached for the $\tilde{A}$ states of NO·CH$_4$[9] and NO·N$_2$.[10]

## II. Computational Details

For He·NO$^+$ and Ne·NO$^+$ the aug-cc-pVXZ basis sets of Dunning and co-workers [X = D, T, Q, and 5 (for He only)] were used,[11] employing the MP2, QCISD, CCSD, QCISD(T), and CCSD(T) level of theory. For Ar·NO$^+$, the aug-cc-pVZX (X = D, T) basis sets were used at the MP2 level of theory, which could be compared to the results obtained in ref 5, which used nonaugmented versions of these basis sets; in addition, the results of these calculations could then be compared to results using effective core potentials (ECPs), which have been suitably augmented, at both the MP2 and QCISD level, described below.

To enable calculations on Kr·NO$^+$ and Xe·NO$^+$ to be performed, it was clear that a different approach would be needed, owing to the large number of electrons, making all-electron calculations impractical. We have used the LANL2DZ augmented ECP[12] previously for calculations on KO$_2$,[13] BBr$_2$, and BI$_2$,[14] and it was found to give very satisfactory results when augmented by a significant number of polarization functions; however, these are tightly bound species, and in order to determine whether the same approach would be suitable here, the LANL2 ECP, suitably augmented, was used to calculate geometries, harmonic vibrational frequencies, and interaction energies of Ar·NO$^+$, to compare to the all-electron results mentioned above. It was found that the augmented ECP results were in excellent agreement with the all-electron results (vide infra), and so calculations using the augmented ECP were performed on Kr·NO$^+$ and Xe·NO$^+$. The augmentation functions used are detailed below. For N and O, either the D95,[15] 6-311+G(3d), or aug-cc-pVTZ basis set was used, as noted below.

All of the theoretical methods used are size-consistent, and the frozen-core approximation was applied in all cases. The majority of the calculations were performed using Gaussian 94;[16] analytical gradients were used where possible for the geometry optimizations. For vibrational frequencies, analytic second derivatives were used, except for the QCISD calculations, for which numerical methods were employed.

In addition, single-point CCSD(T) calculations on He·NO$^+$ and Ne·NO$^+$, employing the aug-cc-pVQZ and aug-cc-pV5Z (He only) basis sets, were performed with MOLPRO.[17]

**He·NO$^+$.** For He, when using the cc-pVXZ (X = D, T, and Q) basis sets in Gaussian 94, no diffuse functions are available to form the aug-cc-pVXZ basis sets, and so a set of diffuse orbitals were added to these as follows: (1) cc-pVDZ: s (0.07); p (0.30); (2) cc-pVTZ: s (0.0522), p (0.1895), d (0.4915); and (3) cc-pVQZ: s (0.0509), p (0.1556), d (0.3397), f (0.7444).

After these calculations, the MOLPRO package was employed for CCSD(T)/aug-cc-pVQZ and CCSD(T)/aug-cc-pV5Z calculations, for which standard diffuse functions are available. For the aug-cc-pVQZ calculations, it was possible to compare the customized basis set used in the Gaussian 94 calculations and the standard basis set, and it was found that the total energy differences were very small [0.8 cm$^{-1}$ at the CCSD(T) level for the He atom].

**Ar·NO$^+$.** Basis A: LANL2DZ + 2d (1.25, 0.41) for Ar; D95 for N, O + 2d [N (1.654, 0.469); O (2.314, 0.645)].

Basis B: LANL2DZ + sp + 2d for Ar [d as for Basis A; sp (0.067)]; D95 for N, O + sp + 2d [d as for Basis A, sp N(0.0639); O (0.0845)].

Basis C: LANL2 + 5s5p3d for Ar (3.0, 1.0, 0.3333, 0.1111, 0.037/8.0, 2.667, 0.8889, 0.2963, 0.988/1.254, 0.418, 0.1393); 6-311+G(3d) for N, O.

Basis D: LANL2 + 5s5p3d2f for Ar [as for Basis C, except 2f (0.9, 0.2571)]; aug-cc-pVTZ for N, O.

**Kr·NO$^+$.** Basis B: LANL2DZ + sp + 2d for Kr [sp (0.07414), d (1.2, 0.4)]; D95 + sp + 2d for N, O [exponents as for Ar·NO$^+$, Basis A].

Basis C: LANL2 + 5s5p3d for Kr [1.3, 0.4333, 0.1444, 0.048, 0.016/3.0, 1.0, 0.3333, 0.1111, 0.037/0.85, 0.24, 0.069]; 6-311+G(3d) for N, O.

Basis D: LANL2 + 5s5p3d2f for Kr [as for Basis C, with f (0.5, 0.12)]; aug-cc-pVTZ for N, O.

An examination of the atomic wave function using the LANL2 + [5s5p] basis set indicated that there was some erratic behavior in the wave function, with successive coefficients oscillating between positive and negative values. It was thus decided to generate a different valence basis set, which was a [6s6p3d2f] basis set, [8,1,1,1,1,1/8,1,1,1,1,1/1,1,1/1,1], with the 3d and 2f basis functions being the same as Basis D, and the inner s and p basis functions being [2.5, 1.25, 0.625, 0.3125, 0.1563, 0.07813, 0.03906, 0.01953] and [3.0, 1.5, 0.75, 0.375, 0.1875, 0.09375, 0.04688, 0.02344], respectively, which were each contracted down to one s and one p function, with the coefficients being taken from an atomic calculation on Kr, using these functions uncontracted. (The exponents for the s and p basis functions were chosen to scan the same valence space as the standard LANL2DZ basis set, in an even-tempered manner.) These two contracted functions were augmented with five s and five p uncontracted functions: (0.85, 0.2575, 0.07805, 0.02365, 0.007167/0.9, 0.2727, 0.08264, 0.02504, 0.007589). This basis set is designated D1, and C1 when the f functions were not used.

**Xe·NO$^+$.** For Xe, as with Kr, it was found that the valence region of the LANL2 + [5s5p] basis set did not seem to be adequate, because again the coefficients of the atomic functions oscillated between positive and negative values as the zeta exponent became more diffuse. A similar procedure was performed as with Kr, which generated a basis set that was adequate to describe the valence space.

Basis C: LANL2 + [5s5p3d] for Xe, where the contraction is given by [8,1,1,1,1/8,1,1,1,1/1,1,1], with the contracted functions coming from the HF calculation noted above, where the exponents were s {[0.9, 0.6, 0.4, 0.2667, 0.1778, 0.1185, 0.07901, 0.05267], 0.5, 0.1515, 0.04591, 0.01391}, p{[1.5, 1.0, 0.6667, 0.4444, 0.2963, 0.1975, 0.1317, 0.08779], 1.2, 0.3636, 0.1102, 0.03339}, d{0.55, 0.1571, 0.04490}; 6-311+G(3d) for N, O.

Basis C1: For Xe, this consisted of the LANL2 core potential, with basis functions as for Basis C, except that an extra set of uncontracted s and p orbitals were added: s (0.004215), p (0.01012), giving a [6s6p3d] valence basis set; 6-311+G(3d) for N, O.

Basis D1: For Xe, this consisted of the LANL2 core potential, with basis functions as for Basis C1, except a pair of uncontracted f functions were added (0.4, 0.1), giving a [6s6p3d2f] valence basis set; aug-cc-pVTZ for N, O.

Thus, the valence basis sets used for Kr and Xe were designed specifically to give a quality at least as good as the basis sets used for Ar, which, as shown below, give excellent agreement with all-electron calculations. The basis set nomenclature was chosen to allow comparison between the different complexes: the same designation implies a basis set of very similar quality.

**TABLE 1: Calculated Equilibrium Geometries and Harmonic Vibrational Frequencies for He$\cdot$NO$^+$ (α Is the He−N−O Bond Angle)**

| method | $r_{NO}$ (Å) | $r_{He-N}$ (Å) | α (°) | $\omega_1$ (cm$^{-1}$) | $\omega_2$ (cm$^{-1}$) | $\omega_3$ (cm$^{-1}$) |
|---|---|---|---|---|---|---|
| MP2/6-311+G* | 1.086 | 3.448 | 57.2 | 16 | 62 | 2161 |
| MP2/aug-cc-pVDZ | 1.096 | 2.848 | 80.9 | 28 | 99 | 2126 |
| MP2/aug-cc-pVTZ | 1.082 | 2.854 | 74.9 | 27 | 112 | 2157 |
| MP2/aug-cc-pVQZ | 1.079 | 2.780 | 83.0 | – | – | – |
| QCISD/aug-cc-pVDZ | 1.077 | 2.811 | 86.5 | 37 | 99 | 2390 |
| QCISD/aug-cc-pVTZ | 1.063 | 2.790 | 84.0 | 29 | 107 | 2422 |

**TABLE 2: Calculated Interaction Energies and BSSE for He$\cdot$NO$^+$ (cm$^{-1}$)**

| method | BSSE$_{Total}$ | BSSE$_{He}$ | BSSE$_{NO^+}$ | Δ*E*(CP) |
|---|---|---|---|---|
| MP2/6-311+G* | 32.6 | 18.7 | 13.9 | 34.4 |
| MP2/aug-cc-pVDZ | 33.8 | 8.0 | 25.8 | 164.5 |
| MP2/aug-cc-pVTZ | 28.4 | 4.4 | 24.0 | 172.3 |
| MP2/aug-cc-pVQZ | 11.0 | 1.9 | 9.1 | 182.3 |
| QCISD/aug-cc-pVDZ | 33.0 | 7.6 | 25.4 | 162.1 |
| MP2/aug-cc-pVDZ$^a$ | 34.8 | 8.8 | 26.0 | 165.5 |
| MP3/aug-cc-pVDZ$^a$ | 34.1 | 8.1 | 26.0 | 160.4 |
| MP4(SDQ)/aug-cc-pVDZ$^a$ | 39.2 | 7.9 | 26.3 | 162.9 |
| QCISD/aug-cc-pVDZ$^a$ | 34.3 | 7.9 | 26.4 | 160.9 |
| CCSD/aug-cc-pVDZ$^a$ | 36.2 | 7.9 | 28.3 | 160.2 |
| QCISD(T)/aug-cc-pVDZ$^a$ | 34.1 | 7.9 | 26.2 | 168.5 |
| CCSD(T)/aug-cc-pVDZ$^a$ | 36.1 | 7.9 | 28.2 | 168.5 |
| MP2/aug-cc-pVTZ$^a$ | 24.2 | 4.4 | 19.8 | 175.5 |
| MP3/aug-cc-pVTZ$^a$ | 23.5 | 4.0 | 19.5 | 170.9 |
| MP4(SDQ)/aug-cc-pVTZ$^a$ | 22.7 | 4.1 | 18.7 | 171.3 |
| MP4(SDTQ)/aug-cc-pVTZ$^a$ | 23.6 | 4.1 | 19.5 | 183.2 |
| QCISD/aug-cc-pVTZ$^a$ | 23.0 | 4.1 | 18.9 | 169.6 |
| CCSD/aug-cc-pVTZ$^a$ | 23.0 | 4.1 | 18.9 | 169.2 |
| QCISD(T)/aug-cc-pVTZ$^a$ | 23.5 | 4.1 | 19.4 | 179.7 |
| CCSD(T)/aug-cc-pVTZ$^a$ | 23.6 | 4.1 | 19.5 | 179.7 |
| MP2/aug-cc-pVQZ$^a$ | 10.6 | 1.9 | 8.7 | 183.5 |
| MP3/aug-cc-pVQZ$^a$ | 8.9 | 1.3 | 7.6 | 178.8 |
| MP4(SDQ)/aug-cc-pVQZ$^a$ | 8.5 | 1.3 | 7.2 | 178.2 |
| QCISD/aug-cc-pVQZ$^a$ | 8.7 | 1.3 | 7.4 | 176.7 |
| CCSD/aug-cc-pVQZ$^a$ | 8.7 | 1.3 | 7.4 | 176.7 |
| QCISD(T)/aug-cc-pVQZ$^a$ | 9.1 | 1.3 | 7.8 | 187.7 |
| CCSD(T)/aug-cc-pVQZ$^a$ | 9.1 | 1.3 | 7.8 | 187.7 |
| MP2/aug-cc-pV5Z$^a$ | 3.8 | 1.0 | 2.8 | 188.1 |
| QCISD/aug-cc-pV5Z$^a$ | 2.9 | 0.6 | 2.3 | 180.4 |
| CCSD/aug-cc-pV5Z$^a$ | 2.6 | 0.6 | 2.0 | 180.3 |
| QCISD(T)/aug-cc-pV5Z$^a$ | 2.8 | 0.6 | 2.2 | 192.0 |
| CCSD(T)/aug-cc-pV5Z$^a$ | 2.7 | 0.6 | 2.1 | 192.1 |

[a] Calculated at the QCISD/aug-cc-pVTZ optimized geometry.

Basis set superposition error (BSSE) was accounted for by performing full counterpoise corrections, according to the Boys and Bernardi scheme.[18]

## III. Results

**He$\cdot$NO$^+$.** *(a) Geometry and Harmonic Vibrational Frequencies.* The results for He$\cdot$NO$^+$ are shown in Tables 1 and 2. As may be seen from Table 1, the cationic complex is calculated to have a skewed T-shaped structure. For the lowest level of theory and smallest basis set (MP2/6-311+G*), the He−N−O angle is 57°; however, the larger basis sets and higher levels of theory yield a larger angle. The calculation using the smallest basis set puts the He on the O side of the molecule, but the calculations performed with the larger basis sets put the He on the N side, consistently. These latter results are in contrast to those of ref 2, where the He atom was calculated to lie on the O side of the NO moiety. In summary, the present results are consistent with the conclusions of refs 3 and 5 and our conclusion is that the best value for the He−N−O bond angle is ∼85°, which puts the He atom on the N side of the NO$^+$ moiety.

The He−N bond length calculated at the MP2/6-311+G* level of theory is significantly longer than that at the highest level of theory, QCISD/aug-cc-pVTZ, and indeed the shorter value appears to be due mainly to the basis set, rather than the level of theory; our conclusion is that the He−N bond length is 2.8 Å. In Jacobi coordinates, our best calculated equilibrium geometry gives a bond length of 2.8 Å, and a bond angle of 83°, with the He on the N side of the NO$^+$ moiety.

These conclusions regarding the geometry are not based upon CP-corrected surfaces (where CP implies the full counterpoise correction). To investigate this further, a point-by-point correction of the energy is required, and then the geometry may be extracted from a fitted potential energy surface. In general, it is to be expected that bond lengths increase after correction for BSSE; however, when angular effects are also present (as here), then the conclusions are not always so clear-cut. In fact, for all of the complexes considered here, CP-corrected surfaces have been generated, and minimum energy geometries and rovibrational levels are presently being calculated.

The harmonic vibrational frequencies (Table 1) are mainly calculated here to confirm that the calculated geometries are minima, and not saddle points. We note in passing that only the QCISD method gives a good value for the NO$^+$ vibrational frequency ($\omega_3$), which is expected to be almost identical with the uncomplexed value of 2376.42 cm$^{-1}$ [19]; also, the NO$^+$ bond length is very close to the experimental value of 1.063 Å at this level of theory—these conclusions hold for all of the Rg$\cdot$NO$^+$ complexes. It is clear that MP2 theory fails to describe NO$^+$ adequately, but describes the intermolecular surface reasonably well. In accord with ref 20 for Ar$\cdot$NO$^+$, we find that for He$\cdot$NO$^+$ it is not the level of theory that is important, so much as the basis set used, once the basis set is reasonable. One final point is that the calculated intermolecular harmonic vibrational frequencies are relatively consistent, but we note that the intermolecular frequencies, yet to be observed, would be significantly anharmonic.

*(b) Interaction Energy.* The results for the interaction energy are given in Table 2 for a variety of methods. As may be seen, the BSSE is a large percentage of the CP-corrected interaction energy, until the aug-cc-pVQZ basis set is used, at which point it drops dramatically. It is significant that even using this very large basis set, the interaction energy does not appear to have converged to the complete basis set limit, although the BSSE clearly has almost converged. Consequently it was decided to perform calculations employing the aug-cc-pV5Z basis set for this complex only, to see whether the interaction energy would be closer to convergence. The results, shown in Table 2, indicate that in fact the aug-cc-pVQZ and aug-cc-pV5Z results are quite close to each other, for the QCISD and CCSD methods (with and without triple excitations), suggesting that these basis sets are close to saturation.

For the sake of simplicity, BSSE (and consequently the interaction energies) for different theoretical methods are compared at the same geometry, which was chosen to be the QCISD/aug-cc-pVTZ-optimized one. Note that the QCISD and CCSD methods lead to almost identical results, and that triple excitations have a significant effect on the interaction energies, increasing the interaction energy by ∼10 cm$^{-1}$, in each case. Overall, although QCISD is a lower level method than CCSD, that difference is not very important for this complex. In addition, the MP2 level of theory (see Table 2), performs rather well for this complex, but this is almost certainly due to a cancellation of errors associated with the truncation of the Møller−Plesset series. To illustrate this more clearly, the results

**TABLE 3: Calculated Equilibrium Geometries and Harmonic Vibrational Frequencies for Ne•NO$^+$ (α Is the Ne−N−O Bond Angle)**

| method | $r_{NO}$ (Å) | $r_{Ne-N}$ (Å) | α (°) | $\omega_1$ (cm$^{-1}$) | $\omega_2$ (cm$^{-1}$) | $\omega_3$ (cm$^{-1}$) |
|---|---|---|---|---|---|---|
| MP2/6-311+G* | 1.086 | 3.102 | 73.8 | 27 | 61 | 2161 |
| MP2/aug-cc-pVDZ | 1.096 | 2.781 | 95.4 | 38 | 82 | 2127 |
| MP2/aug-cc-pVTZ | 1.082 | 2.795 | 88.7 | 40 | 83 | 2157 |
| QCISD/aug-cc-pVDZ | 1.077 | 2.788 | 96.8 | 41 | 82 | 2390 |
| QCISD/aug-cc-pVTZ | 1.063 | 2.810 | 89.2 | − | − | − |

from MP2, MP3, MP4(SDQ), and MP4(SDTQ) are included in Table 2. The summary of these results is that (i) MP3 and MP4(SDQ) give very similar results, (ii) the QCISD and CCSD results are very close to those of MP3 and MP4(SDQ), but the inclusions of triple excitations leads to an increase of the interaction energy (~10 cm$^{-1}$) similar to that ongoing from MP4(SDQ) to MP4(SDTQ); it is clear that triple excitations are an important factor in the accurate calculation of the interaction energy for these species, and (iii) once triples have been included in the QCISD and CCSD calculations, the results are very similar to the MP2 results, which supports the hypothesis that a cancellation of errors leads to the good performance of MP2 theory here. The interaction energies calculated at the MP2 level are consistently only ~4 cm$^{-1}$ lower than the CCSD(T) values, when the same basis set is used, suggesting the MP2 calculations may lead to a fairly reliable surface, at least close to the minimum.

We conclude that results at the CCSD(T)/aug-cc-pV5Z level are reliable, and our best estimate for the interaction energy of the He•NO$^+$ complex is 195 ± 5 cm$^{-1}$; this should be fairly close to the exact value.

**Ne•NO$^+$.** *(a) Geometry and Harmonic Vibrational Frequencies.* The results for the geometry of the Ne•NO$^+$ complex are given in Table 3; as for He•NO$^+$, the conclusion is that the Ne atom lies on the N side of the NO moiety. The Ne−N−O bond angle is again much smaller at the MP2/6-311+G* level of theory, putting the Ne on the O side of the NO moiety; however, on increasing the basis set quality, once more the Ne moves to the other side of the molecule. Our best estimate of the bond angle from these calculations is ~90°, and the bond length is very similar to that in He•NO$^+$, namely 2.8 Å. In Jacobi coordinates, the bond length is 2.9 Å, and the angle is 80°. As for He•NO$^+$, good agreement with experimental values is seen for the NO$^+$ moiety, at the QCISD level.

The harmonic vibrational frequencies are very similar to those of the He•NO$^+$ complex, but as noted before, they are only used as a confirmation that a minimum energy geometry has been reached.

*(b) Interaction Energy.* Table 4 shows the BSSE and interaction energies at a significant number of levels of theory. Again, the BSSE is a reasonable percentage of the CP-corrected interaction energy until the aug-cc-pVQZ basis set is used. Small basis sets, such as the 6-311+G* basis set, are totally inadequate for the calculation of this quantity. Our best value for the interaction energy of Ne•NO$^+$ is 345 ± 10 cm$^{-1}$. Again, both the QCISD and CCSD methods perform almost identically, with triples having an effect of increasing the interaction energy by ~30 cm$^{-1}$. Also as before, the MP2 theory performs to a similar standard as the QCISD(T) and CCSD(T) methods, when the same basis set is employed, although the trend is not as consistent as in the He•NO$^+$ case. The interaction energy does not appear to have converged with basis set, and so the value calculated here must be considered a lower bound, but the calculations on He•NO$^+$ indicate that the aug-cc-pVQZ basis set is close to saturation.

**TABLE 4: Calculated Interaction Energies and BSSE for Ne•NO$^+$ (cm$^{-1}$)**

| method | BSSE$_{Total}$ | BSSE$_{Ne}$ | BSSE$_{NO^+}$ | Δ*E*(CP) |
|---|---|---|---|---|
| MP2/6-311+G* | 145.7 | 74.0 | 71.7 | 92.3 |
| MP2/aug-cc-pVDZ | 80.2 | 46.9 | 33.3 | 256.0 |
| MP2/aug-cc-pVTZ | 61.8 | 39.0 | 22.8 | 326.5 |
| QCISD/aug-cc-pVDZ | 83.9 | 51.3 | 32.6 | 243.3 |
| MP2/aug-cc-pVDZ[a] | 81.3 | 47.0 | 34.3 | 256.0 |
| QCISD/aug-cc-pVDZ[a] | 86.5 | 52.0 | 34.5 | 238.4 |
| CCSD/aug-cc-pVDZ[a] | 84.8 | 50.5 | 34.3 | 235.4 |
| QCISD(T)/aug-cc-pVDZ[a] | 95.7 | 58.5 | 37.2 | 254.7 |
| CCSD(T)/aug-cc-pVDZ[a] | 94.8 | 57.7 | 37.1 | 253.8 |
| MP2/aug-cc-pVTZ[a] | 59.7 | 38.1 | 21.6 | 328.9 |
| QCISD/aug-cc-pVTZ[a] | 61.4 | 40.9 | 20.5 | 309.3 |
| CCSD/aug-cc-pVTZ[a] | 61.2 | 40.8 | 20.4 | 304.6 |
| QCISD(T)/aug-cc-pVTZ[a] | 63.0 | 41.7 | 21.3 | 334.7 |
| CCSD(T)/aug-cc-pVTZ[a] | 62.8 | 41.7 | 21.1 | 333.1 |
| MP2/aug-cc-pVQZ[a] | 36.9 | 27.1 | 9.8 | 338.9 |
| QCISD/aug-cc-pVQZ[a] | 34.6 | 26.4 | 8.2 | 318.0 |
| CCSD/aug-cc-pVQZ[a] | 35.3 | 26.6 | 8.7 | 313.1 |
| QCISD(T)/aug-cc-pVQZ[a] | 34.7 | 26.5 | 8.2 | 346.4 |
| CCSD(T)/aug-cc-pVQZ[a] | 35.4 | 26.7 | 8.7 | 344.7 |

[a] Calculated at the QCISD/aug-cc-pVTZ optimized geometry.

**TABLE 5: Calculated Equilibrium Geometries and Harmonic Vibrational Frequencies for Ar•NO$^+$ (α Is the Ar−N−O Bond Angle)**

| method | $r_{NO}$ (Å) | $r_{Ar-N}$ (Å) | α (°) | $\omega_1$ (cm$^{-1}$) | $\omega_2$ (cm$^{-1}$) | $\omega_3$ (cm$^{-1}$) |
|---|---|---|---|---|---|---|
| MP2/cc-pVDZ[a] | 1.094 | 3.03 | 109.3 | 65 | 109 | 2152 |
| MP2/aug-cc-pVDZ | 1.097 | 2.95 | 105.2 | 81 | 117 | 2121 |
| MP2/cc-pVTZ[a] | 1.083 | 2.97 | 105.6 | 76 | 113 | 2160 |
| MP2/aug-cc-pVTZ | 1.083 | 2.92 | 103.3 | − | − | − |
| MP2/Basis A | 1.100 | 2.93 | 108.3 | 76 | 126 | 2109 |
| MP2/Basis B | 1.098 | 3.01 | 105.0 | 69 | 101 | 2114 |
| MP2/Basis C | 1.084 | 2.94 | 105.2 | 82 | 121 | 2150 |
| QCISD/Basis C | 1.065 | 2.99 | 104.1 | 77 | 111 | 2407 |

[a] From ref 5.

**Ar•NO$^+$.** *(a) Geometry and Harmonic Vibrational Frequencies.* As may be seen from Table 5, and the results quoted in the Introduction, the results obtained using augmented ECP basis sets and all-electron basis sets are in good agreement, for both vibrational frequencies and the complex geometry. Our conclusion from this is that ECPs, when suitably augmented, are able to describe the valence region sufficiently well to allow accurate calculation of these properties for heavier species, such as Kr•NO$^+$ and Xe•NO$^+$. In passing, we note that in ref 5 nonaugmented cc-pVXZ basis sets were used (these are also shown in Table 5, for comparison). The effect, as might be expected, is to shorten the intermolecular bond distance slightly and to increase the intermolecular stretch vibrational frequency, $\omega_2$. The diffuse functions of the augmentation also lead to a slightly smaller bond angle. The best values for the geometric parameters are 104 ± 1° for the Ar−N−O bond angle, and 2.9 ± 0.1 Å for the Ar−N bond length.

*(b) Interaction Energy.* The calculated interaction energies are shown in Table 6. The MP2/aug-cc-pVTZ calculations yield 977 cm$^{-1}$ for the interaction energy, vs 954 cm$^{-1}$ at the highest level of calculation with the augmented ECP basis set. The latter value is in excellent agreement with the value of 950 cm$^{-1}$ calculated in ref 3 at the MP2 level, using a very large basis set, and is also in good agreement with the experimental value of $D_0 = 951$ cm$^{-1}$ [21] (note that the calculated values are $D_e$ values). Because CCSD(T) and QCISD(T) methods appeared to give very similar results for He•NO$^+$ and Ne•NO$^+$, (vide supra), only QCISD(T) calculations were performed for the heavier complexes.

**TABLE 6: Calculated Interaction Energies for Ar·NO$^+$ (cm$^{-1}$)**

| method | $\mathrm{BSSE_{Total}}$ | $\mathrm{BSSE_{Ar}}$ | $\mathrm{BSSE_{NO^+}}$ | $\Delta E^{\mathrm{CP}}$ |
|---|---|---|---|---|
| MP2/aug-cc-pVTZ | 91 | 55 | 36 | 977 |
| MP2/Basis A | 211 | 152 | 60 | 647 |
| MP2/Basis B | 284 | 246 | 38 | 626 |
| QCISD/Basis C | 143 | 103 | 40 | 773 |
| MP2/Basis D//QCISD/Basis C | 189 | 148 | 41 | 985 |
| QCISD/Basis D//QCISD/Basis C | 185 | 146 | 39 | 880 |
| QCISD(T)/Basis D//QCISD/ Basis C | 192 | 152 | 41 | 954 |

**TABLE 7: Calculated Equilibrium Geometry and Harmonic Frequencies for Kr·NO$^+$ (α Is the Kr−N−O Bond Angle)**

| method | $r_{\mathrm{NO}}$ (Å) | $r_{\mathrm{Kr-N}}$ (Å) | α (°) | $\omega_1$ (cm$^{-1}$) | $\omega_2$ (cm$^{-1}$) | $\omega_3$ (cm$^{-1}$) |
|---|---|---|---|---|---|---|
| MP2/Basis B | 1.099 | 3.03 | 110.7 | 78 | 135 | 2102 |
| MP2/Basis C | 1.098 | 2.97 | 109.8 | 92 | 158 | 2136 |
| QCISD/Basis C | 1.066 | 3.03 | 108.6 | 87 | 146 | 2395 |
| QCISD/Basis C1 | 1.066 | 3.07 | 108.6 | 81 | 138 | 2396 |

**TABLE 8: Interaction Energies for Kr·NO$^+$ (cm$^{-1}$) Calculated at the Geometry Optimized at the QCISD/Basis C Level of Theory**

| method | $\mathrm{BSSE_{Total}}$ | $\mathrm{BSSE_{Kr}}$ | $\mathrm{BSSE_{NO^+}}$ | $\Delta E^{\mathrm{CP}}$ |
|---|---|---|---|---|
| MP2/Basis C | 226 | 167 | 59 | 1190 |
| MP2/Basis D | 312 | 257 | 55 | 1359 |
| MP2/Basis D1 | 203 | 146 | 58 | 1333 |
| QCISD/Basis C | 241 | 182 | 59 | 1070 |
| QCISD/Basis D | 314 | 260 | 54 | 1219 |
| QCISD/Basis D1 | 207 | 150 | 57 | 1191 |
| QCISD(T)/Basis D | 326 | 270 | 55 | 1325 |
| QCISD(T)/Basis D1 | 218 | 160 | 58 | 1300 |

**TABLE 9: Calculated Equilibrium Geometry and Harmonic Vibrational Frequencies for Xe·NO$^+$ (α Is the Xe−N−O Bond Angle)**

| method | $r_{\mathrm{NO}}$ (Å) | $r_{\mathrm{Xe-N}}$ (Å) | α (°) | $\omega_1$ (cm$^{-1}$) | $\omega_2$ (cm$^{-1}$) | $\omega_3$ (cm$^{-1}$) |
|---|---|---|---|---|---|---|
| MP2/Basis C | 1.089 | 3.03 | 113.3 | 98 | 207 | 2081 |
| QCISD/Basis C1 | 1.068 | 3.12 | 112.5 | 90 | 185 | 2359 |

**Kr·NO$^+$ and Xe·NO$^+$.** *(a) Geometry and Harmonic Vibrational Frequencies.* The calculated geometries for Kr·NO$^+$ and Xe·NO$^+$ are shown in Tables 7 and 9, respectively. At both the MP2 and QCISD level of theory, using ECP-based basis sets, which have been augmented in a fashion similar to that which has been shown to yield very accurate values for Ar·NO$^+$, consistent results are obtained for the bond angles and the intermolecular bond length. For Kr·NO$^+$, the Kr−N−O bond angle is 108 ± 2°, and for Xe·NO$^+$ it is 112 ± 1°; the bond lengths are both 3.1 ± 0.2 Å.

*(b) Interaction Energies.* As may be seen from Table 8, the interaction energy for Kr·NO$^+$ varies by ∼250 cm$^{-1}$ with the level of theory and the basis set, but the two highest levels are relatively consistent, and agree well with the MP2 calculation with the largest basis set. The best value for the interaction energy of Kr·NO$^+$ is 1310 ± 30 cm$^{-1}$. For Xe·NO$^+$ (Table 10) a similar variation is found, however there are less data on which to base the accuracy of the results, and a best value of ∼1980 cm$^{-1}$ is obtained, but no error range is given. It is clear that the basis set is not saturated here, and so the interaction energies calculated here must be considered lower limits.

## IV. Discussion

**TABLE 10: Interaction Energies for Xe·NO$^+$ (cm$^{-1}$)**

| method | $\mathrm{BSSE_{Total}}$ | $\mathrm{BSSE_{Xe}}$ | $\mathrm{BSSE_{NO^+}}$ | $\Delta E^{\mathrm{CP}}$ |
|---|---|---|---|---|
| MP2/ Basis C | 272 | 195 | 77 | 1802 |
| QCISD/Basis C1 | 262 | 187 | 76 | 1554 |
| MP2/Basis D1//QCISD/Basis C1 | 276 | 220 | 56 | 1979 |
| QCISD/Basis D1//QCISD/Basis C1 | 281 | 220 | 55 | 1790 |
| QCISD(T)/Basis D1//QCISD/ Basis C1 | 299 | 242 | 57 | 1976 |

**BSSE.** The actual BSSE value varies dramatically with the level of calculation, and increases as the size of the rare gas atom increases, but the latter is to be expected because the number of electrons is increasing. A more meaningful comparison is to look at what percentage is the BSSE of the non-CP-corrected interaction energy, for the highest levels of theory in each case: this yields values of 1.3% (He·NO$^+$), 8.5% (Ne·NO$^+$), 16.8% (Ar·NO$^+$), 14.3% (Kr·NO$^+$), and 13.1% (Xe·NO$^+$). Alternatively, one may look at the BSSE per electron in the complex, which gives values of 0.2 cm$^{-1}$ (He·NO$^+$), 1.5 cm$^{-1}$ (Ne·NO$^+$), 8.3 cm$^{-1}$ (Ar·NO$^+$), 9.9 cm$^{-1}$ (Kr·NO$^+$), and 13.6 cm$^{-1}$ (Xe·NO$^+$). These results indicate that for He·NO$^+$ and Ne·NO$^+$, the effects of BSSE are very small, and that the interaction energies, geometries, and vibrational frequencies should be only mildly affected by any residual effects. For Ar·NO$^+$, Kr·NO$^+$, and Xe·NO$^+$, for which an augmented ECP is used, the BSSE is rather more significant. (Note that the ECP does not contribute at all to the ghost center calculations.)

It is interesting to examine the BSSE for NO$^+$ as a function of the basis set on the Rg atom. The most straightforward way is to look at the aug-cc-pVTZ basis set on NO$^+$, with various basis sets on the Rg atoms. For He and Ne, the BSSE for NO$^+$ is ca. 20 cm$^{-1}$, for Ar it is 40 cm$^{-1}$, and for Kr and Xe it is ca. 55 cm$^{-1}$; thus, the aug-cc-pVTZ basis set is not saturating the NO valence space here, and the NO moiety is making use of the orbitals on the Rg center. In fact, this is to be expected because, as the Rg atom becomes heavier, the valence basis functions become more diffuse, and so the NO$^+$ moiety is able to make use of these more readily. When the aug-cc-pVQZ basis set is used, it may be seen from Tables 2 and 4 that the BSSE for NO$^+$ has decreased to ∼8−9 cm$^{-1}$, and is about the same for He·NO$^+$ and Ne·NO$^+$, indicating that this basis set is quite close to saturation.

For Kr·NO$^+$ and Xe·NO$^+$, Tables 8 and 10, it may be seen that the BSSE for NO$^+$ is almost constant at 55−60 cm$^{-1}$, and the majority of the BSSE is associated with the Rg atom, indicating that the ECP basis set is not completely adequate for these species. It would be of great interest to be able to vary the ECP, and determine the effect on the BSSE of the Rg atom, but that is not so straightforward, since different ECPs require different valence basis sets.

For Rg = He, Ne, and Ar, with an all-electron basis set, the behavior of the BSSE in Rg can be understood in the light of the discussion for NO$^+$. With the ECP basis set, for the heavier Rg atoms, the larger BSSE suggests that the ECP basis set is not saturated. The inadequacy seems to be more serious for the heavier Rg atoms, the valence electrons of which occupy a more diffuse orbital space. Although Basis D/D1 is larger than Basis C/C1, the aug-cc-pVTZ basis set on NO$^+$ in the former has more diffuse functions than the 6-311+G(3d) basis set in the latter. Consequently, the BSSE on the Rg atom with Basis D/D1 is larger than that with Basis C/C1.

Despite the weaknesses in the ECP basis sets discussed above, the calculations show that relatively reliable interaction energies can be calculated using this methodology, which is exemplified by the close agreement between the ECP results for Ar·NO$^+$ and the all-electron results. Our conclusions here are that correction for BSSE is certainly necessary to yield a reliable value of the interaction energy. The correction for BSSE should not be used as a means to overcome the weaknesses of a small basis set, however: it may be seen from Tables 2 and 4 that the interaction energy consistently rises as the basis set is increased, *after* correction for BSSE.

**Geometries.** The geometries of these complexes vary quite dramatically in the angular direction, where the best estimates of the Rg-N−O bond angles along the series are 83°, 90°, 104°, 109°, and 113°, for Rg = He to Xe, respectively. Clearly, there is an increasing tendency for the rare gas atom to align itself toward the nitrogen side of the molecule as the size and polarizability increases. The implication of this is that the interaction energy increases in this direction. If the dipole/induced-dipole force is dominant, then a linear geometry is expected; however, if quadrupole/induced-dipole interactions dominate, then a T-shaped geometry results. It is clear that the latter dominates throughout the whole Rg•$NO^+$ series, but that as the Rg atom becomes more polarizable, the former becomes more important, and so starts to pull the Rg atom toward the linear orientation. As noted in ref 5, the $NO^+$ ion has a charge distribution, which has more charge on N than on O, thus the fact that the rare gas atom heads toward the N end of the NO moiety is understandable, since this is where the charge/induced-dipole interaction will be greatest, and the electron−electron repulsion energy will be smallest. For the Rg•CO complexes, the lightest rare gas atom is found to prefer the O end of the molecule, whereas the heavier atoms tend to have a more T-shaped geometry.[22] CO is known to be $^{\delta-}$C−O$^{\delta+}$, and so it appears that the electron−electron repulsion is the dominant effect in determining which linear conformer the complexes prefer.

The most significant point is that the previous determination[2] of the geometries of He•$NO^+$ and Ar•$NO^+$, where the rare gas was concluded to be on the oxygen side of the NO moiety, is incorrect. As noted above (and see Tables 1 and 3), for both He•$NO^+$ and Ne•$NO^+$ small basis sets led to this conclusion. In addition, it is the larger basis sets which leads to the rare gas atom moving to the N side of the molecule. Consequently, as in ref 5, we conclude that the incorrect geometry calculated in ref 2 is a consequence of the small basis set used therein. Some support for this variation in the calculated geometry comes from the Mulliken population analysis. Although it is well known that the populations obtained using this method are basis set dependent, for all but the smallest basis sets used here, they indicated similar results. The results were that for He•$NO^+$, the charge distribution for the NO moiety is $^{0.52+}$O−N$^{0.47+}$ at the MP2/6-311+G* level, whereas this changes to $^{0.12+}$O−N$^{0.88+}$ at the MP2/aug-cc-pVQZ level; very similar values are obtained at the QCISD level; these results are mirrored for Ne•$NO^+$.

Of course, these complexes are fairly floppy, especially the lighter ones, and so the coordinate space sampled by the rare gas atom may be quite large, especially along the angular direction. Consequently, the equilibrium geometry may be significantly different from that deduced from an experiment, although for the heavier complexes, the interaction energy suggests some rigidity; however, the equilibrium geometries are a useful guide to the balance of forces within the complex.

**Interaction Energies.** The interaction energies increase, as expected, as the polarizability of the rare gas atom increases. The values range from a modest 195 $cm^{-1}$ for He•$NO^+$ up to a more significant 1950 $cm^{-1}$ for Xe•$NO^+$. It seems clear that in the case of He•$NO^+$, the bonding is still rather weak, despite the presence of a positive charge on NO, this is probably a result of the small polarizability of He. For Xe•$NO^+$, the interaction becomes rather strong, but is still far from chemical bond strength. As has been noted above, the MP2 method seems to give results comparable in accuracy to the QCISD(T) and CCSD(T) methods. In addition, it has been clearly demonstrated that triple excitations are an important factor here, but the CCSD and QCISD methods both give very similar results, whether triple excitations are included or not.

**Harmonic Vibrational Frequencies.** As mentioned above, the sole reason behind calculating the harmonic vibrational frequencies was to ensure that the calculated geometries corresponded to minima, rather than saddle points. Review of the relevant tables reveals, however, that rather consistent values result. The only complex for which there are experimental values is the Ar•$NO^+$ complex, from the ZEKE photoelectron experiment,[1] mentioned in the Introduction. The values obtained therein were 80.3 and 99.6 $cm^{-1}$ (harmonic values), which compare very favorably with the values in Table 5. Anharmonicity is expected to be important, however, especially for higher vibrational levels; for such an analysis, a potential energy surface needs to be calculated and fitted in order to examine the effects of anharmonicity; this has been performed for Ar•$NO^+$ in refs 3 and 20. Currently, such surfaces for the smaller Rg•$NO^+$ cationic complexes are being calculated, and will be reported at a later date. It is clear from the harmonic levels that, in line with the increased interaction energy, the intermolecular frequencies $\omega_1$ and $\omega_2$ increase as the Rg atom increases in size, with the intermolecular stretch vibration $\omega_2$, increasing more dramatically than the intermolecular bending frequency $\omega_1$.

## V. Conclusions

The Rg•$NO^+$ cationic complexes have been investigated using both all-electron basis sets and augmented ECP basis sets. The augmented ECP basis sets were tested on Ar•$NO^+$ against all-electron basis sets, and found to give good results, although a larger BSSE, probably attributable to the ECP basis set, seemed to imply that some cancellation of errors was occurring. Even so, interaction energies and harmonic vibrational frequencies followed the expected trend, with the overall bonding increasing as the size, and hence polarizability, of the Rg atom increased. The geometries were particularly interesting: they all showed an increase in the Rg−N−O bond angle as the size of Rg increased, with the Rg atom moving toward the N end of the complex. *All* of the complexes had an equilibrium geometry that had the Rg atom on the N side of the complex, at the highest levels of theory. Previous results which indicated that Ar•$NO^+$ and He•$NO^+$ have the Rg atom on the O end of the molecule are thought to be suffering from the effects of an inadequate basis set. It appears that the basis set and not the level of theory is the crucial factor in the description of the geometry of the complexes; for the interaction energies, however, as exemplified by He•$NO^+$, rather demanding calculations are required in order to converge the energy with basis set and method, and it appears that calculations of *at least* QCISD(T)/aug-cc-pVQZ are needed for this complex, especially if it is the region close to the dissociation limit which is of interest. Consequently, the calculation of the potential energy surfaces should be very reliable for He•$NO^+$ and Ne•$NO^+$, because the required level of calculation is practicable, although expensive. For Ar•$NO^+$, the potential energy surfaces of refs 3 and 20 are probably fairly reliable, but for Kr•$NO^+$ and Xe•$NO^+$ probably larger and more flexible valence basis sets are needed, maybe also with a better ECP. If the low vibrational levels are of interest, then lower-level calculations, probably of the MP2/aug-cc-pVTZ standard, should be sufficient.

**Acknowledgment.** The authors are grateful to the EPSRC for the provision of computer time. P.S. would like to thank the Royal Society for the award of a NATO Postdoctoral Fellowship. E.P.F.L. is grateful to the Hong Kong Polytechnic University for support. T.G.W. is grateful to the EPSRC for the award of an Advanced Fellowship.

## References and Notes

(1) Takahashi, M. *J. Chem. Phys.* **1992**, *96*, 2594.

(2) Robbe, J.-M.; Bencheikh, M.; Flament, J.-P. *Chem. Phys. Lett.* **1993**, *210*, 170.

(3) Wright, T. G.; Špirko, V.; Hobza, P. *J. Chem. Phys.* **1994**, *100*, 5403.

(4) Fourré, I.; Raoult, M. *Chem. Phys.* **1995**, *198*, 215. (Note that the pages numbers are misprinted in the journal for this reference.)

(5) Wright, T. G. *J. Chem. Phys.* **1996**, *105*, 7579.

(6) See, for example, Bush, A. M.; Dyke, J. M.; Mack, P.; Smith, D. M.; Wright, T. G. *J. Chem. Phys.* **1998**, *108*, 406.

(7) Bush, A. M.; Dyke, J. M.; Mack, P.; Smith, D. M.; Wright, T. G. *J. Chem. Phys.* **1996**, *105*, 9804.

(8) Mack, P.; Dyke, J. M.; Wright, T. G. *J. Chem. Soc., Faraday Trans.* **1998**, *94*, 629.

(9) Lee, E. P. F.; Mack, P. Wright, T. G. *Chem. Phys.* **1997**, *224*, 191.

(10) Mack, P.; Dyke, J. M.; Smith, D. M.; Wright, T. G. *Chem. Phys. Lett.* **1998**, *284*, 423.

(11) Woon, D. E.; Dunning, T. H., Jr. *J. Chem. Phys.* **1993**, *98*, 1358; Kendall, R. A.; Dunning, T. H., Jr.; Harrison, R. J. *J. Chem. Phys.* **1992**, *96*, 6796; Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007.

(12) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 270, 284, 299.

(13) Lee, E. P. F.; Wright, T. G. *J. Phys. Chem. A* **1988**, *102*, 1036.

(14) Lee, E. P. F.; Wright, T. G. *J. Phys. Chem. A* **1997**, *101*, 1374.

(15) Dunning, T. H., Jr.; Hay, P. J. *Modern Theoretical Chemistry;* Schaefer, H. F., III, Ed.; Plenum: New York, 1976; p 1.

(16) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheesemans, J. R.; Keith, T. W.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94 (Revision C.3)*; Gaussian Inc.: Pittsburgh, PA, 1995.

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

(18) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553.

(19) Huber, K. P.; Herzberg, G. *Molecular Spectra and Molecular Structure IV: Constants of Diatomic Molecules*; van Nostrand: New York, 1979.

(20) Bush, A. M.; Wright, T. G. Špirko, V.; Jurek, M. *J. Chem. Phys.* **1997**, *106*, 4531.

(21) Tsuji, K.; Shibuya, K.; Obi, K. *J. Chem. Phys.* **1994**, *100*, 5441.

(22) Walker, K. A.; Ogata, T.; Jäger, W.; Gerry, M. C. L.; Ozier, I. *J. Chem. Phys.* **1997**, *106*, 7519.