A CCSD(T) study of the HeNO molecular complex

Edmond P. F. Lee and Timothy G. Wright

Related Articles

The divide-expand-consolidate family of coupled cluster methods: Numerical illustrations using second order Møller-Plesset perturbation theory
J. Chem. Phys. 136, 014105 (2012)

Accurate ab initio quartic force fields of cyclic and bent HC2N isomers
J. Chem. Phys. 135, 244310 (2011)

Theoretical characterization of intermolecular vibrational states through the multi-configuration time dependent Hartree approach: The He2,3ICl clusters
J. Chem. Phys. 135, 244309 (2011)

Note: Accurate ab initio predictions of ionization energies of propargyl and allyl radicals: Revisited
J. Chem. Phys. 135, 246101 (2011)

Orbital-optimized third-order Møller-Plesset perturbation theory and its spin-component and spin-opposite scaled variants: Application to symmetry breaking problems
J. Chem. Phys. 135, 224103 (2011)

Additional information on J. Chem. Phys.

A CCSD(T) study of the He·NO molecular complex

Edmond P. F. Lee[a)]

Department of Applied Biology and Chemical Technology, Hong Kong Polytechnic University, Hung Hom, Hong Kong and Department of Chemistry, University of Southampton, Highfield, Southampton, SO17 1BJ United Kingdom

Timothy G. Wright[b)]

Department of Chemistry, University of Southampton, Highfield, Southampton, SO17 1BJ United Kindgdom

Calculations at the CCSD(T) level of theory employing the cc-pVTZ, aug-cc-pVTZ and aug-cc-pVQZ basis sets are reported. Both the $^2A'$ and the $^2A''$ states are considered, as well as the two linear structures, He·NO and He·ON. The highest level of calculation, CCSD(T)/aug-cc-pVQZ//CCSD(T)/aug-cc-pVTZ, indicates that the global minimum is a skewed T-shaped structure, in agreement with recent CEPA calculations, but in disagreement with MP4 calculations, which concluded that the linear He·ON isomer was the lowest energy geometry. Although the highest level of theory used here indicates that the $^2A'$ surface is the lower in energy, the ordering of the $^2A'$ and the $^2A''$ surfaces has not yet been firmly established. The interaction energy is calculated to be $\sim$27 cm^{-1}, and estimated as being $\sim$30 cm^{-1} at the basis set limit. © *1998 American Institute of Physics.* [S0021-9606(98)01525-6]

I. INTRODUCTION

Recently, as part of an experimental program into the study of Rg·NO complexes (Rg=rare gas),[1] the known dissociation energies of the ground states of these species were collated. These have been reported in the literature as 172 cm^{-1} (He·NO, Abstract of Ref. 2); 88 cm^{-1} (Ar·NO, Ref. 3); 110 cm^{-1} (Kr·NO, Ref. 4); and 121 cm^{-1} (Xe·NO, Ref. 1), where all but the value for He·NO are derived from experiment. It thus became quickly apparent that the dissociation energy for He·NO reported in the Abstract of Ref. 2 was questionable. At this point Ref. 2 was examined in more detail, which revealed that there had been a misprint in the Abstract of Ref. 2, and that the reported interaction energy should have been 17.2 cm^{-1}.

At this juncture, it is necessary to consider the bonding of the He·NO complex in more detail. NO has a $^2\Pi$ ground state, and thus when a helium atom interacts with a NO molecule, the $^2\Pi$ state can split into a $^2A'$ and a $^2A''$ state, depending on whether the unpaired electron is in-plane or out-of-plane. Recently, a CEPA study on the $^2A'$ and $^2A''$ states by Yang and Alexander[5] has been reported; a grid of energy points was calculated, and fitted to a potential in order to derive scattering data. Yang and Alexander[5] considered both surfaces, and concluded that the $^2A'$ surface was slightly more repulsive that the $^2A''$ one, and that both surfaces had a minimum in a near perpendicular orientation, implying an almost T-shaped geometry. It is interesting to note that for Ar·NO, a similar geometry has been established by Howard and co-workers[6] by radio-frequency and microwave spectroscopy, which is also consistent with the CEPA

calculations of Alexander,[7] where again the $^2A'$ surface was slightly more repulsive than the $^2A''$ one. The results of Ref. 5 for the minimum energy geometry of He·NO are contrary to the MP4//MP2 study by Zolotoukhina and Kotake,[2] who concluded that the global minimum on the He/NO potential energy surface was at a linear orientation, He·ON. (For the nonlinear structures studied, it is not clear whether the $^2A'$ or $^2A''$ surface was considered.) No comment was made in Ref. 5 concerning the different conclusion in Ref. 2, and in addition, only a contour plot of the potential energy surface was presented in Ref. 5, and no minimum energy geometry nor interaction energy was given. Both studies considered basis set superposition error (BSSE), with Yang and Alexander performing a point-by-point correction, and Zolotoukhina and Kotake using a single-point correction at calculated stationary points. Although the latter authors went into some depth in their consideration of the magnitude and source of the BSSE, the former authors did not give any indication of its size. One interesting aspect of BSSE in such weakly-bound systems is its variation with geometry, and so a minimum on a surface that has been corrected for BSSE might not be the same as that on the uncorrected surface. Further, the size and effect of spin-contamination in unrestricted wave functions needs to be addressed; in both of the aforementioned studies, it was not stated whether unrestricted wave functions were used, and if so, whether spin-contamination was a problem. Also both of the previous studies used single-reference methods, and so a check on whether such methods are adequate for this complex is necessary.

Some other aspects of Refs. 2 and 5, which we wanted to explore in greater depth, were as follows:

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

(i)   What is the global energy minimum structure of He·NO, and what is the electronic state, if the minimum is nonlinear?

(ii)   What is the effect of basis set on the optimized geometry, BSSE and interaction energy? Although this was addressed in Ref. 2, the basis sets used were still rather small, being based on the 6-311+G basis sets with variation of the polarization function space; this is indicated by the large BSSEs, compared to the interaction energy. Reference 5 on the other hand employed the large aug-cc-pVQZ basis sets of Dunning and co-workers,[8] with the majority of the calculations excluding the g functions, but did not comment on the basis set effect nor the size of the computed BSSE.

(iii)   What is the effect of BSSE on the calculated geometry and the interaction energy? As noted above, Ref. 5 performed a point-by-point counterpoise correction. Reference 2 considered the BSSE in some detail; they noted that the BSSE they were calculating was much larger than the interaction energy itself, but concluded that the calculated interaction energy was stable with basis set, mainly by considering the energy changes on the helium atom, when the s space was thought to be saturated. It might be expected, however, that the major BSSE would be associated with the NO molecule, rather than the He atom, since NO has more electrons, and has electronegative atoms. Thus, the basis set variation performed in Ref. 2 may not be adequate. Also the differential effect of BSSE on the calculated minimum energy geometry is of interest, with two linear ($^2\Pi$) and two T-shaped ($^2A'$ and $^2A''$) to be considered. (In all cases, including here, the full counterpoise method is employed.)

(iv)   What is the effect of higher levels of theory? Use of the MP4 energy at the MP2 optimized geometry (as used in Ref. 2) may not be adequate for a description of this complex. Also the CEPA method (used in Ref. 5) is an approximate coupled-cluster method,[9] and so the use of a better technique, such as CCSD(T) would be informative.

II. THEORETICAL METHODS

In order to address the points noted above, the following procedure was adopted.

The geometry was optimized at the CCSD(T) level of theory employing numerical energy gradients, using the cc-pVTZ and aug-cc-pVTZ basis sets, where both the $^2A'$ and the $^2A''$ states were considered, as well as the two linear isomers: He·ON and He·NO (both $^2\Pi$). Then aug-ccpVTZ//cc-pVTZ and aug-cc-pVQZ//aug-cc-pVTZ single-point energy calculations were performed.

Unrestricted wave functions were employed in all cases. The CCSD(T) method was selected since it is one of the best single-reference methods available. To ensure that a single-reference was sufficient to describe this complex, CISD and MRCISD calculations were performed. The CCSD(T) approach is a higher-level of theory than the CEPA approach, and has the advantage over CASSCF and MRCI approaches

in that the choice of the reference space is not a consideration—this can become problematic when considering different electronic states, and also in the full counterpoise (CP) correction methodology for BSSE. Geometry optimizations were started at linear geometries and T-shaped for both the $^2A'$ and $^2A''$ states. All of these surfaces were extremely flat, so that even when the energy changes were much less than 1 cm^{-1} during the geometry optimization, the geometry was still changing, indicating a very flat surface, indicated by gradients $<10^{-5}$ atomic units; since it is the energetics which were of primary interest here, once the energy had converged to <1 cm^{-1}, the optimization was stopped. No attempt to calculate second derivatives was made, because the severe flatness of these surfaces would make the vibrational frequencies obtained from such calculations unreliable, especially with numerical methods, since these are all based on the harmonic approximation.

For He, augmentation functions for the cc-pVTZ and cc-pVQZ basis sets are not available in GAUSSIAN 94, and so a set of even-tempered diffuse functions were designed as follows:

cc-pVTZ: $s(0.0522); p(0.1895); d(0.4195)$,

cc-pVQZ: $s(0.0509); p(0.1556); d(0.3397); f(0.7444)$.

These were obtained using ratios of 4.0 and 3.6, extending from the most diffuse exponent in the underlying basis set.

For the MRCI calculations a 6-311G* basis set was used; this was augmented with the following diffuse and polarization functions:

He: $s(0.0509); p(3.0, 0.1875); d(2.76)$,

N: $sp(0.0639); d(3.196, 0.261); f(1.093)$,

O: $sp(0.0845); d(4.522, 0.369); f(1.428)$.

All CCSD(T) calculations were performed using GAUSSIAN 94;[10] the CI calculations were performed using GAMESS-UK.[11]

III. RESULTS AND DISCUSSION

A. MRCISD calculations: Validity of single-reference and UHF-based methods

A reference space for the MRCISD calculations was generated by continually extending the results from a single-reference CISD calculation, until all significant contributing configurations were included, giving a total of 12 references; ~7 million CSFs were generated for the optimized bent geometries (see below) and also for a bond length of 200 Å; for the linear geometries, 3.5 million configurations were generated, since only half of the states may be included in the D_{2h} symmetry used for the calculations. In all cases $\Sigma c_i^2 > 0.91$, with the largest $c_i > 0.93$, indicating that a single reference wave function is adequate for this complex. The calculated binding energies from these calculations, using the supermolecule approach, were very much higher than those calculated using the CCSD(T) approach (vide infra) and were, in fact, of a similar magnitude to the MP4//MP2 results reported in Ref. 2, with no BSSE correction; in particular the He·ON linear isomer was the lowest in energy. The poor

TABLE I. Calculated energetics of the He·NO complex at the CCSD(T) level of theory.

Basis set	Orientation and state[a]	$-(E_{tot}+132)/E_h$	Rel E_{tot}/cm^{-1}	ΔE_e/cm^{-1}	He$_{BSSE}$/cm^{-1}	NO$_{BSSE}$/cm^{-1}	BSSE$_{tot}$/cm^{-1}	ΔE_e(CP)/cm^{-1}
cc-pVTZ								
	He·NO bent $^2A''$	0.6171211	0.00	−12.31	1.84	19.38	21.22	+8.91
	He·NO linear $^2\Pi$	0.6171206	0.09	−12.22	2.17	7.99	10.16	−2.06
	He·ON linear $^2\Pi$	0.6171175	0.77	−11.55	1.65	4.46	6.10	−5.44
	He·NO bent $^2A'$	0.6171192	0.42	−11.90	1.45	13.89	15.34	+3.45
aug-cc-pVTZ// cc-pVTZ								
	He·NO bent $^2A''$	0.6268441	1.62	−26.69	1.29	7.16	8.45	−18.23
	He·NO linear $^2\Pi$	0.6268515	0.00	−28.31	1.32	10.97	12.29	−16.02
	He·ON linear $^2\Pi$	0.6268346	3.73	−24.58	0.99	6.15	7.14	−17.45
	He·NO bent $^2A'$	0.6267938	12.66	−15.65	0.88	4.78	5.66	−9.99
aug-cc-pVTZ								
	He·NO bent $^2A''$	0.6268606	4.13	−30.27	2.09	9.48	11.57	−18.70
	He·NO linear $^2\Pi$	0.6268644	3.34	−31.10	1.80	13.96	15.76	−15.34
	He·ON linear $^2\Pi$	0.6268794	0.00	−34.39	2.15	14.66	16.81	−17.58
	He·NO bent $^2A'$	0.6268745	1.19	−33.21	1.67	8.03	9.70	−23.51
aug-cc-pVQZ// aug-cc-pVTZ								
	He·NO bent $^2A''$	0.6607464	4.78	−27.57	0.72	3.53	4.25	−23.33
	He·NO linear $^2\Pi$	0.6607413	5.90	−26.47	0.81	7.99	8.80	−17.67
	He·ON linear $^2\Pi$	0.6607455	4.98	−27.39	0.90	6.01	6.91	−20.48
	He·NO bent $^2A'$	0.6607682	0.00	−32.37	0.75	4.68	5.42	−26.95

[a]For geometries, see Table II.

performance of the MRCISD and MP4//MP2 results, compared to those using the CEPA and CCSD(T) methods, are attributed to the following points: (i) the smaller basis set used; (ii) the limited account of electron correlation, as compared to CCSD(T); and (iii) the lack of correction for BSSE. (We note that for the MRCISD calculations it is not easy to ensure that a consistent configurational space is used for all of the calculations necessary for a full CP correction to be made.)

In addition, for all of the calculations reported here, $\langle S^2 \rangle \sim 0.8$, indicating that spin contamination of the unrestricted wave functions was not significant; this is also exemplified by the similar results obtained here using the MRCISD approach, which employed restricted wave functions, compared with the MP4//MP2 results of Ref. 2, which presumably used unrestricted wave functions. Consequently, we conclude that the use of the CCSD(T) method ought to give reliable results.

B. BSSE

One of the main weaknesses of the work of Zolotoukhina and Kotake[2] was the fact that the calculated BSSE was much larger than the interaction energy, although some attempt at justifying the final results was made. As may be seen from Table I, using the cc-pVTZ basis set, the BSSE is still greater than the CP-corrected interaction energy; even using the aug-cc-pVTZ basis set, the BSSE is about the same size. It is only when the aug-cc-pVQZ basis set is used that the BSSE becomes reasonable. The conclusion from this is clearly that basis sets of at least aug-cc-pVQZ quality are needed to obtain meaningful interaction energies; thus, the basis sets used in Ref. 2 are too small.

As may be seen from Table I, CP correction for BSSE changes the relative energy ordering of the different structures (compare columns 4 and 9 in Table I). This change in ordering arises since the calculated BSSE is different for different orientations; this is in addition to the general expectation that increasing the bond length decreases the BSSE. Clearly, since the energy differences between different orientations is rather small, then even quite small changes in the relative BSSEs can change the overall energy ordering, when based on the CP-corrected energies. It is noted that the use of small basis sets in calculations on He·NO$^+$ and Ar·NO$^+$ in Ref. 12 has been attributed[13] as being the probable cause of an incorrect calculated geometry. In addition, it is our view that the CP correction should not be used as a "quick fix" to overcome the deficiencies of an inadequate basis set, although the analysis of wave functions of CP calculations involving ghost orbitals can sometimes indicate what the weaknesses in a basis set are.[14] Certainly it would appear to be at least desirable for the BSSE to be less than the CP-corrected interaction energy in order to make reliable conclusions; as may be seen from Table I, using the aug-cc-pVQZ basis set, the BSSE is ~0.5 cm^{-1} per electron, and is not expected to be decreased to any significant extent with a larger basis set. The effect that BSSE has on the interaction energy and minimum energy geometry of the He·NO complex is examined in more detail in the following subsection, but a general observation is that the BSSE of the two linear structures appears to behave similarly, as does that of the two bent structures, with basis set variation.

C. Global minimum energy structure

Employing the cc-pVTZ basis set, all four structures are almost isoenergetic. After CP-correction, the situation

changes significantly, in particular the two bent structures become unbound, owing to the large BSSE, whereas the linear structures are still bound, but only very weakly. At the aug-cc-pVTZ//cc-pVTZ level before CP correction, the He·NO linear configuration becomes the lowest energy geometry; once CP correction has been made, the bent $^2A''$ surface becomes the lowest.

Once geometry optimization has been performed using the aug-cc-pVTZ basis set, then the He·ON linear geometry is the global minimum before the CP correction, while the bent $^2A'$ becomes the lowest after CP correction. In this case, in contrast to the cc-pVTZ results, the two linear structures have the largest BSSEs, which leads to an alteration in the global minimum structure.

At the highest level of theory used here, aug-cc-pVQZ//aug-cc-pVTZ, the $^2A'$ surface is the lowest both before and after CP correction, and the energy ordering remains unchanged. As in the aug-cc-pVTZ//aug-cc-pVTZ case, the two linear structures have the largest BSSEs, although here the difference in BSSEs between the linear and bent cases is significantly smaller. A question may reasonably be asked at this point as to whether a full optimization at the aug-cc-pVQZ level, or indeed employing larger basis sets, would alter the calculated minimum. To test the former, the energy at the geometries of the last few iterations in the aug-cc-pVTZ optimization were calculated using the aug-cc-pVQZ basis set, and these indicated that the curvature of the aug-cc-pVQZ surface, both before and after CP correction, was very similar to that of the aug-cc-pVTZ surface, and so would lead to a similar minimum energy geometry; within the computing resources available to us, this is as far as it is possible to check these results.

Note that the ordering of the $^2A'$ and the $^2A''$ surfaces obtained here is reversed from that of Ref. 5, where the CEPA approximation was used, despite the fact that the basis set used therein was very similar to that used here. For Ar·NO, Alexander,[7] again using the CEPA method, also calculated the $^2A''$ surface to be lower than the $^2A'$ surface (and both linear structures). This conclusion is in agreement with the microwave study of Howard and co-workers,[6] who were able to determine the Renner-Teller parameter, ϵ, as -2.68 cm^{-1}; the sign indicated that the $^2A''$ surface was the lower. In his calculations on Ar·NO (Ref. 7), Alexander used the aug-cc-pVTZ basis set of Dunning. Note that for He·NO from Table I, at the CCSD(T)/aug-cc-pVTZ level of theory, the $^2A'$ surface is lower than the $^2A''$ one, and this result is unchanged using the aug-cc-pVQZ basis set. It seems clear that for energy differences of only a few cm^{-1}, this is at the limit of the accuracy of *ab initio* calculations. Our conclusion at present is that the evidence for the $^2A''$ surface's being lower than the $^2A'$ one for Ar·NO is persuasive; however, for He·NO, it is not so clear. An experimental determination of ϵ for He·NO would decide the ordering of the two surfaces.

It is also worth pointing out that in Ref. 5 the energy of a He atom approaching collinearly was calculated, giving a minimum energy at a Jacobi bond length of 3.97 Å, $(-18.54$ cm$^{-1})$ for a He·NO approach, and 3.70 Å $(-23.43$ cm$^{-1})$ for a He·ON approach; these compare to

TABLE II. Geometry of the last optimized point (see text for details); bond lengths in Å, angles in degrees.

Basis set	cc-pVTZ	aug-cc-pVTZ
Bent He·NO ($^2A''$)		
He-N	3.3595	3.2323
N-O	1.1530	1.1532
∠HeNO	116.8	95.2
Linear He·NO ($^2\Pi$)		
He-N	3.3987	3.2120
N-O	1.1530	1.1532
Linear He·ON ($^2\Pi$)		
He-O	3.3980	2.9948
N-O	1.1530	1.1531
Bent He·NO ($^2A'$)		
He-N	3.5534	3.3155
N-O	1.1530	1.1531
∠HeNO	117.4	74.8

values of 3.75 Å $(-17.67$ cm$^{-1})$ and 3.61 Å $(-20.48$ cm$^{-1})$ here, respectively, with the geometries obtained at the CCSD(T)/aug-cc-pVTZ level and the energies at the CCSD(T)/aug-cc-pVQZ//CCSD(T)/aug-cc-pVTZ level (where Jacobi bond lengths are referred to in all cases). An *estimation* of the calculated minimum energy geometry from a contour plot in Ref. 5, yields Jacobi bond lengths and angles of 3.3 Å, 60° ($^2A''$) and 3.3 Å, 100° ($^2A'$). For the $^2A''$ surface, this implies a He-N bond length of 3.0 Å and ∠HeNO=110°, while for the $^2A'$ surface, the corresponding values are 3.5 Å and 70°; it may be seen that these values compare favorably with the values calculated with the aug-cc-pVTZ basis set (Table II), especially the bond angles. It is also interesting to see that these are similar to the values for Ar·NO calculated by Alexander[7] at the CEPA/aug-cc-pVTZ level of theory, where for the $^2A'$ surface, the corresponding values were 3.8 Å and 77°, while for the $^2A''$ surface they were 3.6 Å and 98°. The very good agreement between the surface of Ref. 5 and the results here give added weight to the conclusions of both papers. It therefore seems clear that the conclusions of Ref. 2, in which the calculated global minimum was a linear He·ON geometry, are not correct.

The shallowness of the potential energy surface will mean that the geometry of the molecule may be difficult to define, since large amplitude motions of the He atom will be occurring, even with just the zero-point energy present; thus, the r_e structures presented in Table II are probably not meaningful as far as an experiment is concerned. In addition, the barriers to linearity are 6.5 and 9.3 cm^{-1}, for the N and O ends, respectively, as calculated at the aug-cc-pVQZ//aug-cc-pVTZ level, including CP corrections; thus, with zero-point energy, this complex will be at least very close to a free rotor. In addition, it is probable that the angular momentum of the NO molecule is only very weakly quenched by the presence of He: in Ar·NO, the angular momentum quenching was found to be small.[6,15] Finally, it is pleasing that the calculated r_{NO} distances (1.153 Å) are very close to the experimental r_e value of 1.15077 Å (Ref. 16) (this distance was assumed in Ref. 5).

The binding energy of the $^2A'$ surface at the highest level of theory used here, CCSD(T)/aug-cc-pVQZ//

CCSD(T)/aug-cc-pVTZ level of theory, is 27 cm^{-1}, but we note from the trend in values, that this will probably be larger at the basis set limit, probably giving a value of $\sim$30 cm^{-1}.

IV. CONCLUSIONS

Calculations at the CCSD(T) level, the highest level of theory so-far used, employing large basis sets, conclude that the minimum energy geometry of the He$\cdot$NO complex is a skewed T-shaped structure. This is in agreement with recent CEPA calculations, using similar basis sets, although the ordering of the $^2A'$ and $^2A''$ surfaces is reversed, with the $^2A'$ being calculated to be the lower here. These conclusions together indicate that the conclusions of a recent MP4//MP2 study, in which the He$\cdot$ON linear geometry was calculated to be the global minimum, are in error. The highest level of calculation employed here indicates that the complex is bound by $\sim$30 cm^{-1}; clearly zero-point energy implies that the dissociation energy, D_0, will be smaller than this value, making this a very weakly bound complex. It has not yet been observed experimentally (see Ref. 1).

ACKNOWLEDGMENTS

[1] P. Mack, J. M. Dyke, and T. G. Wright, J. Chem. Soc., Faraday Trans. **94**, 629 (1998).

[2] T. N. Zolotoukhina, and S. Kotake, J. Chem. Phys. **99**, 2855 (1993).

[3] K. Tsuji, K. Shibuya, and K. Obi, J. Chem. Phys. **100**, 5441 (1994).

[4] A. M. Bush, J. M. Dyke, P. Mack, D. M. Smith, and T. G. Wright, J. Chem. Phys. **105**, 9804 (1996).

[5] M. Yang and M. H. Alexander, J. Chem. Phys. **103**, 6973 (1995).

[6] P. D. A. Mills, C. M. Western, and B. J. Howard, J. Phys. Chem. **90**, 4961 (1986).

[7] M. H. Alexander, J. Chem. Phys. **99**, 7725 (1993). R. A. Kendall, T. H. Dunning, Jr., and R. J. Harrison, *ibid.* **96**, 6796 (1992); T. H. Dunning, Jr., *ibid.* **90**, 1007 (1989).

[8] A. Szabo and N. S. Ostlund, *Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory* (McGraw–Hill, New York, 1982).

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

[10] M. F. Guest and J. Kendrick, GAMESS User Manual, SERC Daresbury Laboratory, CCP1/86/1, U.K.

[11] J.-M. Robbe, M. Bencheikh, and J.-P. Flament, Chem. Phys. Lett. **210**, 170 (1993).

[12] T. G. Wright, J. Chem. Phys. **105**, 7579 (1996).

[13] T. G. Wright, J. M. Dyke, and E. P. F. Lee, Mol. Phys. **73**, 941 (1991).

[14] B. J. Howard, C. M. Western, and P. D. Mills, Discuss. Faraday Soc. **73**, 129 (1982).

[15] K. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure IV. Constants of Diatomic Molecules* (Van Nostrand Reinhold, New York, 1979).