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Theoretical study of PO and PO⁻*

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The diatomic systems, PO and PO^- are studied, using numerical Hartree-Fock (NHF) and coupled-cluster calculations. The latter employs a hybrid NHF and Slater orbital basis set. Highly accurate CCSD methods predict bond lengths accurate to <0.004 Å and frequencies to ~60 cm^{-1}. In addition the electron affinity of PO is computed to be 0.89 eV compared to an experimental value of 1.09±0.01. Comparisons are made with SCF and MBPT(2) results for PO^+ using conventional basis sets.

Key words: Quantum chemistry — *Ab initio* — Electron correlation — Coupled-cluster theory — Numerical Hartree-Fock — Structure and spectra — PO — PO^-

1. Introduction

The infrared spectroscopy of organophosphorous compounds is of considerable interest for a number of reasons, including their importance in the identification of chemical agents and simulants [1]. These spectra are often dominated by the strong P=O stretching mode. A number of correlations have been made for this vibration, based on experimental studies of these compounds [2]. We are beginning a study [3] of these compounds to try to develop some theoretical basis, from *ab initio* quantum-mechanical calculations, for further understanding of these relationships. It appears worthwhile to begin a systematic study of $R_3P{=}O$ and $R_3P{=}S$ compounds by a high-level study of just the diatomic PO and PS compounds themselves. Some effect of substituents on these compounds may be

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* Dedicated to Professor J. Koutecký on the occasion of his 65th birthday

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simulated by calculating properties of the positive and negative ions PO^+, PO^-, PS^+ and PS^-.

These diatomic radicals and ions have some interesting properties and applications in themselves; for example, the PO radical is generated in excimer laser photofragmentation of organic phosphorous compounds [4] and PO^- has been studied by laser photoelectron spectrometry [5]. All the ions and radicals except for PS^- have been studied spectroscopically, and their ground state vibrational frequencies and bond distances are summarized by Huber and Herzberg [6].

An earlier *ab initio* quantum-mechanical study has been made by Lohr at the SCF level using a 6-31G* basis set [7] for PO and PO^-. However, we considered the possibility that the vibrational properties of PO and PS compounds in general might not be predicted adequately just by SCF theory for this kind of basis set. Consequently, we decided to carry out a detailed investigation into the basis set dependence and correlation dependence of our predicted vibrational properties of these compounds. This may be accomplished by obtaining very accurate results using the numerical Hartree-Fock method [8] with correlation effects calculated by means of the coupled cluster method (CC) [9].

In this first part of our study we shall present the numerical HF calculations for PO and PO^-. We shall present the corresponding calculations for the PS diatomic series elsewhere.

2. Numerical procedure

In this initial study our research goal is to perform very accurate calculations on the potential energy surfaces for the PO molecule and its anion, PO^-, in order to establish a sound theoretical prediction for the electron affinity, the $0 \rightarrow 1$ vibrational transition energies and some spectroscopic parameters. The computational technique employed involves the numerical Hartree-Fock (HF) method for diatomic systems, augmented by Slater orbitals to describe the virtual orbitals with electron correlation treated at the Coupled Cluster level CCSD+T(CCSD) [10].

The numerical HF and MCSCF [8] programs for diatomic systems are used to generate spin-adapted ROHF wave functions for the ($^2\Pi$) ground state of PO and the $^3\Sigma$ PO^- ion at several internuclear distances. Numerical orbitals generated by these programs are expressed in prolate spheroidal coordinates as the following partial wave expansions:

$$\psi_n(\zeta, \eta, \phi) = \sum_{L=|m|}^{L_n} X_{nL}^m(\zeta) Y_L^m(\eta, \phi) \qquad (1)$$

where the Y_l^m are the spherical harmonics and the X_{nL}^m are numerical functions which are determined by solving the HF equations. The subscript m denotes the orbital symmetry ($m = 0$ for σ orbitals, $m = \pm 1$ for π symmetry etc.). The results of the numerical ROHF calculation for PO and PO^- are presented in Table 1.

Table 1. Numerical HF results for PO and PO$^-$ at experimental equilibrium geometries (for PO: $R_e = 1.476$ Å; for PO$^-$: $R_e = 1.540$ Å)

	PO $^2\Pi[1\sigma^2 2\sigma^2 3\sigma^2 1\pi^4 4\sigma^2 5\sigma^2 6\sigma^2 2\pi^4 7\sigma^2 3\pi^1]$	PO$^-$ $^3\Sigma[1\sigma^2 2\sigma^2 3\sigma^2 1\pi^4 4\sigma^2 5\sigma^2 6\sigma^2 2\pi^4 7\sigma^2 3\pi^2]$
Orbital energies [a.u.]		
1σ	−80.02826	−79.73487
2σ	−20.58099	−20.28822
3σ	−7.56566	−7.27099
1π	−5.45706	−5.16360
4σ	−5.45673	−5.16319
5σ	−1.34722	−1.04427
6σ	−0.73498	−0.46247
2π	−0.53960	−0.26272
7σ	−0.53790	−0.25599
3π	−0.32383	−0.06657
Total HF energy [a.u.]		
	−415.62985	−415.65613
Dipole moment [debye]: (calculated with respect to the center of the molecular positive charge for PO$^-$):		
	2.599	−0.613

The next step in our procedure is the mapping of numerical HF orbitals obtained for the equilibrium geometries onto a space of Slater functions using the procedure described previously [11]. Such a technique has also been used for atomic calculations by Beck and Nicolaides [12]. This procedure is chosen in order to develop the functional space for correlated calculations using the MBPT or CC methods. Using a hybrid NHF and Slater basis is a computationally simpler alternative than the purely numerical bases we have used before [13]. Since the electron attachment process usually causes a significant diffusion of the wave function to get the best possible result, we have chosen to use different basis sets for the calculation of the anion and the neutral system. The projection of the numerical HF orbitals for PO and PO$^-$ onto Slater functions resulted in two different Slater orbital sets. The principle and angular quantum numbers as well as the initial exponents for the Slater orbitals for P and O atoms have been taken from the calculations of Cade [14]. Our optimal exponents for PO and PO$^-$ are presented in Table 2.

Upon examination of the Slater orbital sets it is clear that the π set for the anion consists of more diffuse functions than the set for the neutral. However, this feature is not that transparent for the σ set, which is clearly a reflection of the fact that the reaction $\mathrm{PO} + e^- \rightarrow \mathrm{PO}^-$ is a π-type attachment process. In Fig. 1 the highest two σ and π PO and PO$^-$ orbitals are presented and the comparison indicates that the wave function undergoes a greater expansion in the π region.

The present study of the basis set requirements for the calculation on the covalent electron attachment process has a broader meaning. It shows how to shape the basis set of atomic orbitals for an electron affinity calculation.

Table 2. Slater orbital basis sets for PO and PO$^-$ obtained by mapping the numerical HF wave functions onto Slater functions

	PO (R_e = 1.476 Å)	PO$^-$ (R_e = 1.540 Å)
	Exponents	
σ orbitals		
P: 1s	17.439198	16.994003
$2s$	15.139205	15.085733
$3s$	1.371490	1.135030
$3s$	2.213572	2.124026
$3s$	8.815809	8.728164
$2p_0$	10.494838	11.364103
$2p_0$	4.847127	4.830617
$2p_0$	4.208452	4.289645
$2p_0$	6.370993	6.817324
$3p_0$	1.365161	1.299588
$3p_0$	2.256643	2.153315
$3d_0$	2.267876	2.021716
$4f_0$	2.455746	2.220711
O: $1s$	12.643636	12.041797
$1s$	6.944258	6.766174
$2s$	1.478132	1.693713
$2s$	2.667609	2.821423
$3s$	8.690475	8.326987
$2p_0$	2.474494	4.863401
$2p_0$	1.256432	1.205844
$2p_0$	0.962248	1.531649
$2p_0$	4.976559	2.330158
$3d_0$	1.389967	1.017964
$3d_0$	2.380025	2.207445
$4f_0$	2.611349	2.514191
π orbitals		
P: $2p_1$	9.405517	8.433210
$2p_1$	3.722828	1.750345
$2p_1$	5.338905	4.587115
$2p_1$	1.022873	0.732816
$3p_1$	1.857814	1.485553
$3d_1$	1.582703	1.529539
$4f_1$	2.028541	1.920109
O: $2p_1$	2.162977	1.961603
$2p_1$	0.904229	0.645373
$2p_1$	1.006120	0.900319
$2p_1$	4.441326	4.092772
$3d_1$	2.545345	2.677079
$4f_1$	0.927696	0.800661

In the present calculations we use basis sets which consist of HF numerical orbitals and Slater functions. The only varying component of the basis set is the subset of the numerical orbitals, which is determined for each nuclear distance in a separate ROHF calculation. The unchanged Slater orbital subsets for PO and PO$^-$ have been developed based upon the Slater representation of the HF numerical orbitals described earlier. This has been done by removing functions with larger exponents and adding higher momentum functions (d and f). For those additional orbitals the exponents of the σ and π sets have been used. This procedure results in a set of 28 primitive Slater functions (distributed as 13σ, 9π, 4δ and 2ϕ), of which all virtual orbital combinations have been retained in the correlated calculations.

The idea behind this procedure for basis set construction is to develop a set of functions, which enables the best possible description of the electronic structure for both the neutral and the anion at the HF level, which, presumably will provide an adequate functional space for the *valence* electron correlation. The latter is clearly the most important type of correlation for the electron attachment process under study.

The composite of numerical HF orbitals and Slater orbitals is eventually used to perform correlated calculations using the CC method with single and double excitations (CCSD) [15] and its extension, the CCSD+T(CCSD) method [10], including the linear contribution from triple excitations calculated from converged CCSD amplitudes. It has been shown [16] that the CCSD+T(CCSD) method provides the total electronic energy with an accuracy that differs from the full CI result by less than one kcal/mol in the proximity of the equilibrium geometry.

The CC method utilizes the following exponential ansatz for the wave function:

$$\Psi_{CC} = e^{\mathcal{T}}\psi_{HF} \tag{2}$$

with the reference function ψ_{HF} being the HF determinant and the CC operator $\mathcal{T}$ consisting of one-, two-, three-, etc. electron operators:

$$\mathcal{T} = \mathcal{T}_1 + \mathcal{T}_2 + \mathcal{T}_3 + \cdots \tag{3a}$$

$$\mathcal{T}_1 = \sum_{i,a} t_i^a a_a^\dagger a_i \tag{3b}$$

$$\mathcal{T}_2 = \sum_{i>j,a>b} t_{ij}^{ab} a_a^\dagger a_i a_b^\dagger a_j \tag{3c}$$

$$\mathcal{T}_3 = \sum_{\substack{i>j>k\\ a>b>c}} t_{ijk}^{abc} a_a^\dagger a_i a_b^\dagger a_j a_c^\dagger a_k, \tag{3d}$$

where $i, j, k, \ldots$ and $a, b, c, \ldots$ refer to occupied and virtual orbitals respectively. An iterative procedure for finding the CC amplitudes, t, and CC energy has been described before [9].

In the present calculation we employ ROHF reference determinants resulting from numerical HF calculations. However, unlike the basis set SCF procedure the numerical HF approach generates no virtual orbitals. The purpose of adding Slater orbitals to the ROHF numerical solutions is to generate a virtual orbital space for expanding the CC correlated wave function. The orthogonality of the virtual orbitals to occupied orbitals has been accomplished by transforming Slater orbitals into partial wave expansions (see Eq. (1)) and then orthogonalizing them to all HF numerical orbitals with the usual projection procedure. The resulting

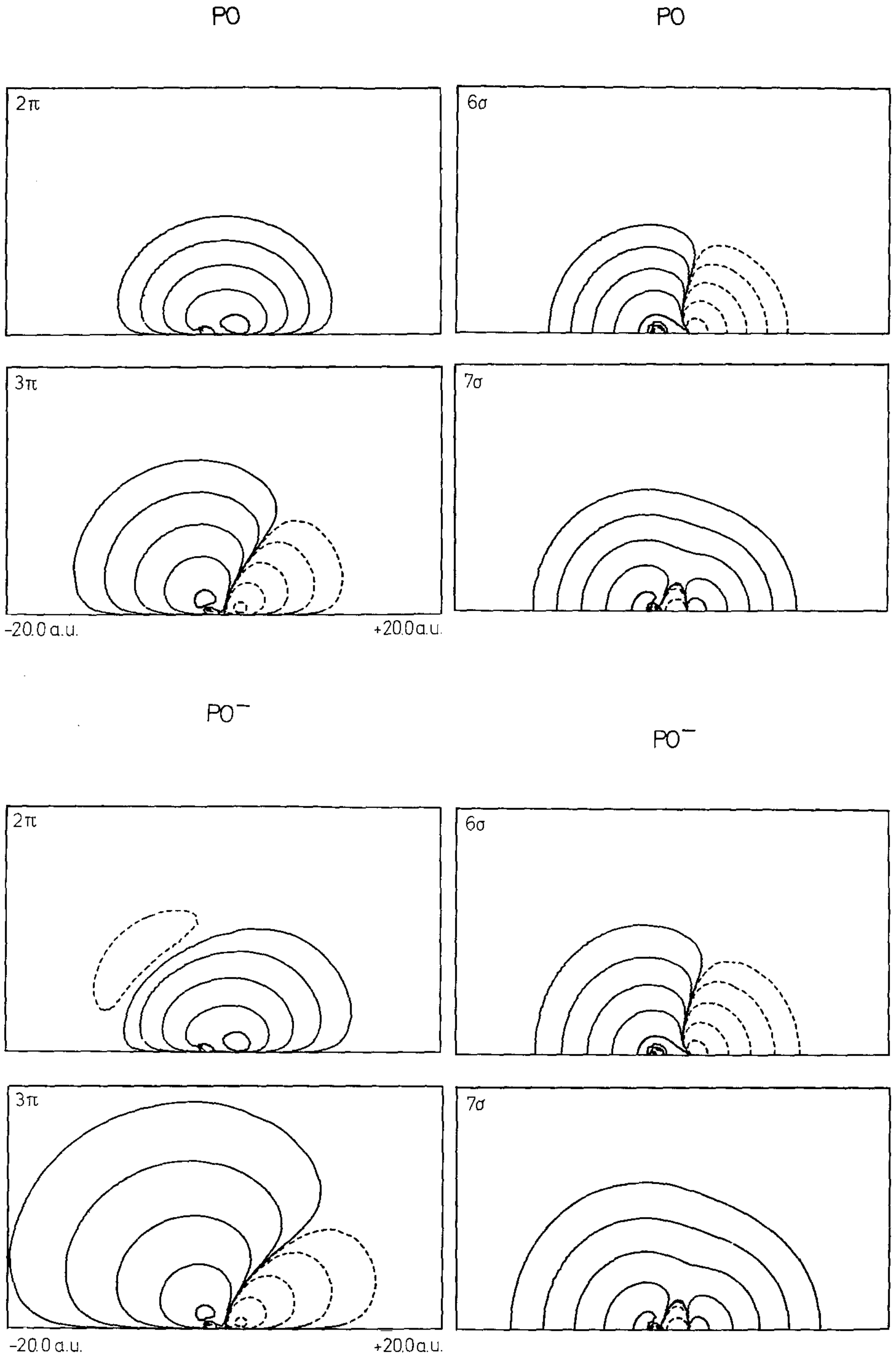

Fig. 1. Contours of the two highest occupied numerical HF orbitals of σ and π symmetry for the PO molecule and the PO^- anion

set of numerical orbitals has been transformed further by forming an overlap matrix and diagonalizing it. The resulting orthogonal vectors, being linear combinations of occupied-space-orthogonal numerical representations of Slater orbitals have been numerically contracted. The following equation explains the contraction procedure:

$$\psi'_a = \sum_a c'_{aa}\psi_a = \sum_{L=|m|}^{L_n} \Big(\sum_a c'_{aa} X^m_{nL,a}(\zeta)\Big) Y^m_L(\eta, \phi) \tag{4}$$

$$= \sum_{L=|m|}^{L_n} X^{m'}_{nL,a}(\zeta)\, Y^m_L(\eta, \phi).$$

The numerical contracts form a new set of numerical orbitals, which span the virtual space. The virtual set is not canonical while the occupied space corresponds to an ROHF solution with orbitals that are maximally doubly occupied, constituting a spin-eigenfunction. This new version of the CC method, termed open-shell spin restricted CC, has been discussed in another study [17]. This paper and reference [17] are the first reports of CC results with this method. This procedure differs from the usual approach, which utilizes the UHF determinant as the CC reference function and differentiates the α and β electron distributions already at the HF level [9]. The UHF reference is not a spin eigenfunction, which persists to some degree through the CCSD+T(CCSD) calculation. However, in practice, CC theory generally improves upon the UHF multiplicity to nearly give a spin-eigenfunction at convergence at least for most open shell cases [18]. The MBPT results reported are based upon a UHF reference.

In the present CC calculations we have chosen to keep the electrons occupying the 1σ, 2σ, 3σ and 1π orbitals uncorrelated. This simplifies the calculation and should not significantly affect the results.

Table 4. Spectroscopic parameters for PO and PO$^-$ in ground electronic states. Calculated results in comparison with experimental data

Method	B_e[cm^{-1})	α_e[cm^{-1}]	ω_e[cm^{-1}]	$\omega_e x_e$ [cm^{-1}]
PO $^2\Pi$				
Numerical HF	0.778	0.0037	1447	7.3
CCSD	0.735	0.0048	1286	6.4
CCSD+T(CCSD)	0.720	0.0056	1197	7.5
Experiment[a]	0.7337	0.0055	1233.34	6.56
PO$^-$ $^3\Sigma$				
Numerical HF	0.716	0.0055	1190	4.3
CCSD	0.678	0.0053	1076	5.7
CCSD+T(CCSD)	0.666	0.0060	1025	7.8
Experiment[b]	0.674[c]	—	1000 ± 70	—

[a] [6]

[b] [5]

[c] Calculated from R_e given by [5]

Table 3. Structural parameters calculated for PO, PO^-, and PO^+ in comparison with experimental data

Present results						Literature results	
	Numerical HF	CCSD	CCSD+T(CCSD)	UHF/DZP	MBPT(2)/DZP	UHF/6-31G*[a]	Experiment
Equilibrium geometry R_e [Å]:							
PO^+	—	—	—	1.396	1.466	—	—
PO	1.433	1.474	1.490	—	—	1.456	1.476370 (15)[b]
PO^-	1.493	1.536	1.548	1.534	1.582	1.528	1.540 ± 0.010[c]
Vibrational transition energy (0→1) [cm^{-1}]:							
PO^+	—	—	—	1654	—	—	1405[d]
PO	1434	1273	1182	—	—	1406	1220.249001 (43)[b]
PO^-	1180	1064	1008	1156	993	1166	1000 ± 70[c]

[a] [7]

[b] Butler JE, Kawaguchi K, Hirota EJ (1983) J Mol Spect 101:161

[c] [5]

[d] Dressler K (1955) Helv Phys Acta 28:563; see also [6]

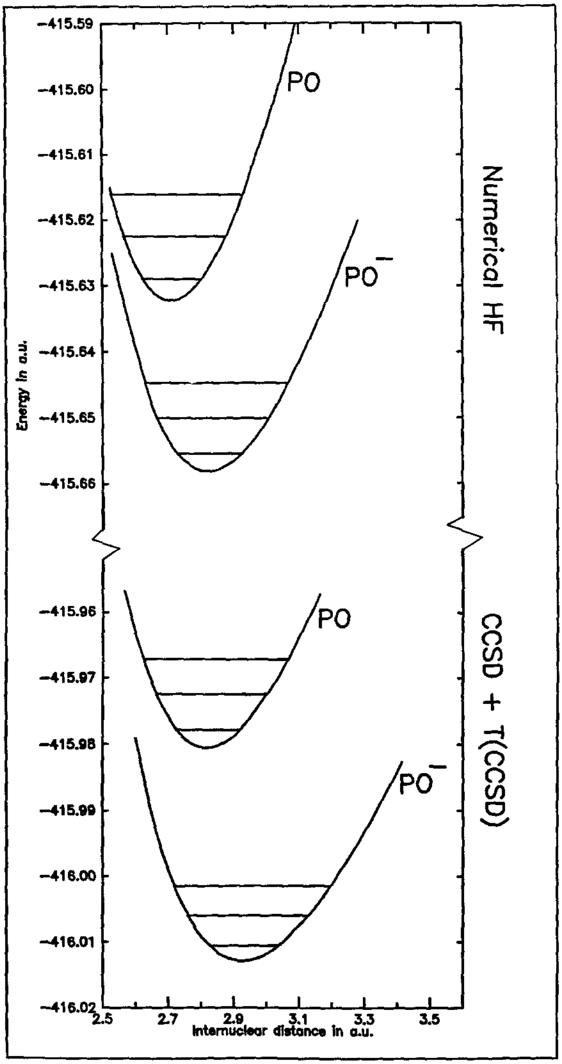

Fig. 2. Potential energy curves for the PO molecule and the PO$^-$ anion calculated with the numerical HF method and CCSD+T(CCSD) method

3. Results

Calculations for the potential energy curves for PO and PO$^-$ have been performed at the HF, CCSD and CCSD+T(CCSD) levels, while some lower level results for PO$^+$ are also reported. For each potential energy curve, 12 points were calculated, and a polynomial fit was made for the vibrational analysis. Results for the zero-order vibrational transition energies and equilibrium internuclear distances and spectroscopic constants are presented in Table 3 and Table 4. Potential energy curves are shown in Fig. 2 and electron affinities calculated at different levels of the theory are given in Table 5.

Table 5. Adiabatic electron affinities for the PO molecule

Method	EA (eV]
Present results:	
Numerical HF	0.70
CCSD	0.91
CCSD+T(CCSD)	0.88
CCSD+T(CCSD)+ vib. correction[a]	0.89
Literature results:	
Calculated:	
MBPT D(3)[b]	0.84
CISD[b]	0.80
Experiment[c]	1.092 ± 0.010

[a] Electron affinity evaluated as a difference of CCSD+T(CCSD) vibrational levels for PO and PO^-

[b] [7]

[c] [5]

The equilibrium nuclear separation for both PO and PO^- evaluated at the CCSD level agrees perfectly with the experimental data. The introduction of the triple excitations in an approximate fashion through the CCSD+T(CCSD) method flattens the potential energy surfaces for PO and PO^- causing an increase of the P–O separation and a lowering of the oscillation levels.

The experimental vibrational frequency for the PO molecule falls between the CCSD and CCSD+T(CCSD) values, as does the value for R_e. However, the bracket is not very tight. It is reasonable to believe that the PO^- ground state frequency lies between the CCSD value of $1064\,\mathrm{cm}^{-1}$ and CCSD+T(CCSD) value of $1008\,\mathrm{cm}^{-1}$. This is consistent with the experimentally established bracket of $1000 \pm 70\,\mathrm{cm}^{-1}$, and with the agreement for R_e.

Our prediction for the electron affinity of the PO molecule differs from the experimental value by 0.20 eV. The inclusion of the triple excitations does not alleviate the discrepancy. It is possible that the basis set we are using is still significantly incomplete or there are some higher connected excitations (the CC method accounts for the disconnected excitations) which are important. One cannot also eliminate some possibility of an error in the experimental electron affinity. Although we have obtained extremely accurate electron affinities for F [13a], LiH [13b], and some other cases, we have similar residual errors of about 0.2 eV for O and NH [19], pointing to some inaccuracy in the treatment of affinities even with purely numerical basis sets. At present we do not have an adequate explanation for this. Certainly the possibility of important multi-reference character is suggested by each example.

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References and notes

1. Hoffland LD, Piffath RJ, Bouck JB (1985) Opt Eng 24:983
2. Thomas LC, (1974) Interpretation of the infrared spectra of organophosphorus compounds. Heyden, London
3. The first paper in this series is: Person WB, Kwiatkowski JS, Bartlett RJ (1987) J Mol Struct 157:237
4. Sausa RC, Miziolek AW, Long SR (1986) J Phys chem 90:3994; see also Long SR, Sausa RC, Miziolek AW (1976) Chem Phys Lett 117:505
5. Zittel PF, Lineberger WC (1976) J Chem Phys 65:1236
6. Huber KP, Herzberg G (1979) Molecular spectra and molecular structure. IV. Constants of diatomic molecules. Van Nostrand Reinhold, New York
7. Lohr LL (1984) J Phys Chem 88:5569
8. McCullough EA (1975) J Chem Phys 62:3991; Adamowicz L, McCullough EA (1981) J Chem Phys 75:2475; Adamowicz L, McCullough EA (1983) Int J Quantum Chem 24:19
9. Bartlett, RJ (1981) Annu Rev Phys Chem 32:359 and references therein; Bartlett RJ, Purvis GD (1978) Int J Quantum Chem 14; Bartlett RJ, Purvis GD (1980) Phys Scripta 21:255
10. Urban M, Noga J, Cole S, Bartlett RJ (1985) J Chem Phys 83:4041
11. Adamowicz L, Bartlett RJ (1986) Chem Phys Lett 129:159
12. Beck D, Nicolaides C (1978) In: Beck D, Nicolaides C (eds) Excited states in quantum chemistry. Reidel, Dordrecht, Holland, p 105
13. Adamowicz L, Bartlett RJ (1986) J Chem Phys 84:6837; Adamowicz L, Bartlett RJ (1985) J Chem Phys 83:6268
14. Cade PE, (1967) Proc Phys Soc 91:842; Cade PE (1967) J Chem Phys 47:2390
15. Purvis GD, Bartlett RJ (1982) J Chem Phys 76:1910
16. Cole, SJ, Bartlett RJ (1987) J Chem Phys 86:873
17. Rittby M, Bartlett RJ, J Phys Chem, in press
18. Purvis G, Sekino H, Bartlett RJ, to be published
19. Adamowicz L, Bartlett RJ, to be published