

Theoretical Study of the Electronic and Geometrical Structure of the Ground and Low-Lying States of NCl_2 , PCl_2 , NCl , and PCl Radicals

Aristotle Papakondylis and Aristides Mavridis*

Laboratory of Physical Chemistry, Department of Chemistry, National and Kapodistrian University of Athens, Panepistimiopolis, Athens 15771, Greece

Aristophanes Metropoulos

Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation, 48 Vassileos Constantinou Avenue, Athens 11635, Greece

Received: January 31, 1995; In Final Form: April 27, 1995[⊗]

Using a variety of *ab initio* methods, SCF, CISD, MP2, MP4, MCSCF, and MCSCF+1+2, we have studied the electronic and geometrical structure of the ground and low-lying states of the isovalent radicals NCl_2 , PCl_2 and NCl , PCl . In particular, we have examined the states $\tilde{X}^2\text{B}_1$, $\tilde{A}^2\text{A}_1$, $\tilde{B}^2\text{B}_2$, $\tilde{C}^2\text{A}_1$, $\tilde{D}^2\text{A}_2$ and $\tilde{X}^2\text{B}_1$, $\tilde{A}^2\text{A}_1$, $\tilde{B}^2\text{B}_2$, $\tilde{C}^2\text{A}_1$, $\tilde{D}^2\text{B}_2$, $\tilde{E}^2\text{A}_2$ for NCl_2 and PCl_2 , respectively. These calculated manifolds can be proved useful in elucidating the complicated electronic spectroscopy of the triatomic species. For the diatomic molecules we have examined the states $\text{X}^3\Sigma^-$, $\text{a}^1\Delta$, and $\text{b}^1\Sigma^+$, while, for the ground $\text{X}^3\Sigma^-$ state only, we constructed full energy potential curves in an effort to obtain accurate dissociation energies.

Introduction

The present work concerns the *ab initio* study of the isovalent molecules dichloroaminy, NCl_2 , and dichlorophosphinyl, PCl_2 , as well as the diatomic isovalent species chloronitrene, NCl , and chlorophosphinedene, PCl , by SCF (self consistent field), CISD (configuration interaction with single and double replacements), MCSCF (multiconfiguration self consistent field), MCSCF+1+2 (multiconfiguration self consistent field plus single and double replacements), and MP2 and MP4 (Møller–Plesset second- and fourth-order perturbation theory) techniques. This study can be considered as a continuation of our work on the NF_2 radical.¹

The NCl_2 molecule was first identified thirty years ago by Briggs and Norrish² by flash photolysis of an NCl_3 – Cl_2 mixture. Since then the experimental work performed on this molecule has been rather limited,³ and as far as we know structural results for the ground and low-lying excited states are essentially lacking in the literature. On the theoretical side, the existing works are those of Hincheliffe and Bounds⁴ at the SCF-UHF level and the very recent work of Austen et al.⁵ on the ground states of the NX_2 and PX_2 systems, $\text{X} = \text{H}, \text{F}, \text{and Cl}$, at the density functional theory (DFT) level.

The existence of the PCl_2 radical has been assumed as early as 1945 by Kharasch et al.,⁶ who were the first to report radical-induced addition of phosphorus trichloride to alkenes via the addition of the dichlorophosphinyl free radical to alkenes.⁷ Since the experimental work of Andrews and Frederick⁷ on PCl_2 the number of experimental studies on this system does not abound.⁸ Theoretical results have been reported very recently by Brum and Hudgens,⁹ who did MP2/6-31G* calculations on the ground $\tilde{X}^2\text{B}_1$ state of PCl_2 , by Gutsev,¹⁰ who examined the $\text{PCl}_n/\text{PCl}_n^-$ series, $n = 1-6$, by the local spin density approximation (LSDA), and by Austen et al. (DFT).⁵

The diatomic species NCl and PCl are photolytic products of the NCl_3 ¹¹ and PCl_3 ⁸ vapors, respectively. The interest on diatomic species like NX or PX , where X can be either F or Cl , is due to their possible use in laser systems.^{1,12} The bond

lengths and spectroscopic constants of both NCl and PCl species are very accurately known from the extensive microwave and infrared laser spectroscopic studies of Hirota and co-workers.^{13–17} On the contrary, the dissociation energy for either species is not so accurately known (*vide infra*). In the recent past, NCl had been the subject of some sophisticated *ab initio* calculations. Lievin and Metz¹⁸ did MCSCF calculations including corrections for higher excitations, Bettendorf and Peyerimhoff¹⁹ presented multireference configuration interaction (MRDCI) energy potential curves for the three lowest ($\text{X}^3\Sigma^-$, $\text{a}^1\Delta$, and $\text{b}^1\Sigma^+$) and a number of higher states of NCl employing the augmented DZ+P quality basis set, and Peterson and Woods²⁰ calculated the ground $\text{X}^3\Sigma^-$ state of NCl at the CISD, MP4SDQ, CEPA-1, and CASSCF levels, using fairly large basis sets. It is interesting that only the calculations by Peterson and Woods produced a bond length favorably comparable with the experimental value, while the best¹⁹ (estimated) dissociation energy is ~80% of the experimental value. Theoretical calculations for PCl have been reported by Nguyen²¹ at the MP2 and MP4/6-31G* levels, by Gutsev¹⁰ at the LSDA level, and, for both species, by Curtiss et al.²² at the Gaussian-1 and Gaussian-2 levels of theory.

In what follows we present *ab initio* calculations using relatively large basis sets and a variety of techniques on all four aforementioned species. The purpose of the present work is to obtain accurate structural and electronic characteristics of the ground and low-lying states, such as energy gaps and dissociation energies, D_e and D_0 . The dissociation energies are obtained only for the diatomic species through the complete potential energy curves. In addition and whenever possible the present study tries to make an assessment among different methodologies.

Basis Sets and Computational Methods

Through all our calculations and for all atoms, the cc-pVTZ basis sets of Dunning^{23,24} were employed contracted according to Raffanetti.²⁵ For the N atom this is a 10s6p2d1f set contracted to 4s3p2d1f while, for the P and Cl atoms, the corresponding basis is (15s9p2d1f) → [5s4p2d1f]. For our triatomic PCl_2 and the diatomic PCl the resulting basis contains

[⊗] Abstract published in *Advance ACS Abstracts*, June 1, 1995.

117 and 78 contracted Cartesian Gaussian functions. The SCF energies of N, P, and Cl atoms in this basis set are $-54.397\ 36$, $-340.715\ 98$, and $-459.478\ 25$ hartrees, respectively, 3.6, 2.7, and 3.6 mhartrees higher than their corresponding Hartree–Fock limits. In all correlated calculations the $\sim 1s^2$ electrons of N and the $\sim 1s^2 2s^2 2p^6$ electrons of P and Cl were considered as core and kept frozen at the SCF level.

The computational methods employed in the present study are SCF, MP2, MP4(STDQ), CISD(+Davidson corrections), MCSCF, and MCSCF+1+2. All our CISD calculations were performed with the MELD²⁶ program, while for the MP n calculations the GAUSSIAN92²⁷ suite of codes was used. The ground state potential curves of NCl and PCl were obtained through MCSCF and MCSCF+1+2 calculations using the COLUMBUS²⁸ set of codes.

Our calculations were performed with the SPARCstation 10 and the Alpha AXP 300X workstations of the Physical Chemistry Laboratory, as well as the CONVEX 3820 computer of the National Center for Scientific Research, DEMOKRITOS, Greece.

Description of the Molecules

NCl₂. The ground state of NCl₂ is given by the configuration

$$|\tilde{X}^2B_1\rangle = \dots(2a_2)^2(8a_1)^2(9a_1)^2(7b_2)^2(3b_1)^1$$

and can be characterized as a π radical, with the symmetry-carrying electron localized on the N atom (we follow here the usual convention: $x \rightarrow b_1$, $y \rightarrow b_2$, $z \rightarrow a_1$). Within this description, orbitals $8a_1$ and $7b_2$ can be considered as the two N–Cl “bonds” of the system. The $9a_1$ orbital can be thought of as the lone pair on the nitrogen atom, and the transferring of an electron from $9a_1$ to $3b_1$ gives rise to the first excited 2A_1 state, clearly a σ -radical:

$$|\tilde{A}^2A_1\rangle = \dots(2a_2)^2(8a_1)^2(9a_1)^1(7b_2)^2(3b_1)^2$$

Three more low-lying states have been tackled, namely:

$$|\tilde{B}^2B_2\rangle = \dots(2a_2)^2(8a_1)^2(9a_1)^2(7b_2)^1(3b_1)^2$$

$$|\tilde{C}^2A_1\rangle = \dots(2a_2)^2(8a_1)^2(9a_1)^2(7b_2)^2(10a_1)^1$$

$$|\tilde{D}^2A_2\rangle = \dots(2a_2)^1(8a_1)^2(9a_1)^2(7b_2)^2(3b_1)^2$$

The computational methods applied to all the above five states are SCF, CISD, MP2, and MP4.

PCl₂. The following six states were studied for this isovalent to NCl₂ system:

$$|\tilde{X}^2B_1\rangle = \dots(2a_2)^2(8b_2)^2(10a_1)^2(11a_1)^2(4b_1)^1$$

$$|\tilde{A}^2A_1\rangle = \dots(2a_2)^2(8b_2)^2(10a_1)^2(11a_1)^2(12a_1)^1$$

$$|\tilde{B}^2B_2\rangle = \dots(2a_2)^2(8b_2)^2(10a_1)^2(11a_1)^2(9b_2)^1$$

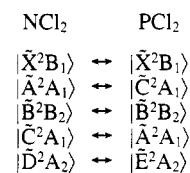
$$|\tilde{C}^2A_1\rangle = \dots(2a_2)^2(8b_2)^2(10a_1)^2(11a_1)^1(4b_1)^2$$

$$|\tilde{D}^2B_2\rangle = \dots(2a_2)^2(8b_2)^1(10a_1)^2(11a_1)^2(4b_1)^2$$

$$|\tilde{E}^2A_2\rangle = \dots(2a_2)^1(8b_2)^2(10a_1)^2(11a_1)^2(4b_1)^2$$

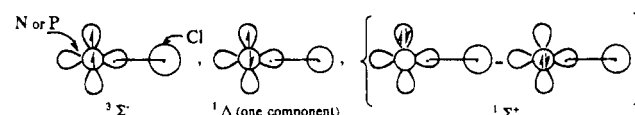
As in the case of NCl₂, in its ground state the PCl₂ is a π -radical. The symmetry-carrying electron is localized on the P atom and is distributed perpendicularly to the plane of the molecule. Notice though that the first excited \tilde{A}^2A_1 state of this species arises in a different manner than that of NCl₂; i.e., it stems from

a $4b_1 \rightarrow 12a_1$ rather than a $11a_1 \rightarrow 4b_1$ electron transfer. The following level correspondence can be drawn between the states of the two (isovalent) systems:



All states were studied by SCF and CISD methods, while states \tilde{X}^2B_1 , \tilde{C}^2A_1 , and \tilde{D}^2B_2 were also studied by MP2 and MP4 techniques. For purely technical reasons we were unable to study the states \tilde{A}^2A_1 , \tilde{B}^2B_2 , and \tilde{E}^2A_2 by the perturbation methods.

NCl and PCl. The lowest energy electron distributions for chloronitrene and chlorophosphinedene are given by the configurations $\dots 5\sigma^2 6\sigma^2 7\sigma^2 2\pi^4 3\pi^2$ and $\dots 7\sigma^2 8\sigma^2 9\sigma^2 3\pi^4 4\pi^2$, respectively. The π^2 distribution gives rise to three molecular terms, namely ${}^3\Sigma^-$, ${}^1\Delta$ and ${}^1\Sigma^+$ (in ascending order) with the following pictorial representations:



For both molecules, the above states were studied at the CISD level; the MP2 and MP4 techniques were used for the $X^3\Sigma^-$ symmetry only. In addition, full potential curves were constructed for the ground states at the MCSCF+1+2 level. The MCSCF space is comprised of 91 configuration state functions, resulting by allowing all excitations from the valence spaces, $5\sigma^2 6\sigma^2 7\sigma^2 2\pi^4 3\pi^2$ and $7\sigma^2 8\sigma^2 9\sigma^2 3\pi^4 4\pi^2$, to the $8\sigma^*$ and $10\sigma^*$ virtual orbitals, respectively. In essence, these MCSCF wave functions can be thought of as 2×2 GVB vectors, i.e. (core)-(core) ($\sigma^2 - 0.1\sigma^{*2}$), the ~ 0.1 coefficient being the largest in the MCSCF expansion. Our MCSCF wave functions are size consistent,^{29,30} dissociating into the ground state SCF atoms, N or P(⁴S) + Cl(²P), thus clearly discerning the nondynamical from the dynamical correlation. The latter is taken into account by allowing all single and double excitations from the MCSCF space (MCSCF+1+2), resulting in an approximately 1 600 000 configuration space. The MCSCF+1+2 functions are size consistent within 10–12 mhartrees of the energy sum of the CISD atomic wave functions, with the sum of the latter being lower than their asymptotic products. By extrapolating to the “full” CI (F-CI) via the Davidson³¹ formulas, our results are size extensive within 1 mhartree.

Results and Discussion

Tables 1 and 2 present all our results on the triatomic species NCl₂ and PCl₂, respectively, while Tables 3 and 4 present results on the diatomic molecules NCl and PCl. Figures 1 and 2 give schematic representations of the energy levels along with geometries of the NCl₂, NCl and PCl₂, PCl molecules, respectively, according to the CISD results (Tables 1 and 2).

Figures 3 and 4 show potential energy curves of the NCl and PCl species in their $X^3\Sigma^-$ states at the MCSCF, MCSCF+1+2, and F-CI levels. By fitting the calculated points to a seventh degree polynomial up to an interatomic distance of about 2.5 Å and using standard perturbation techniques,³² we have obtained molecular constants (Table 5). Expressed in inverse centimeters, the approximate level formula used is given by the expression

TABLE 1: Bond Distances R_e (Å), Bond Angles (deg), Energy Differences ΔE (eV) with Respect to the Ground State, Dipole Moments μ (D), Net Mulliken Charges q , Overlaps S , and Binding Energies BE (kcalmol⁻¹) of the NCl₂ Molecule in the Ground \tilde{X}^2B_1 and Low-Lying States and in Different Methodologies

	\tilde{X}^2B_1						\tilde{A}^2A_1						\tilde{B}^2B_2					
	SCF	CISD	MP2	CI-Q ^a	F-CI ^a	MP4	SCF	CISD	MP2	CI-Q ^a	F-CI ^a	MP4	SCF	CISD	MP2	CI-Q ^a	F-CI ^a	MP4
R_{N-Cl}	1.688	1.688	1.691	1.704	1.712	1.710	1.633	1.634	1.636	1.645	1.649	1.652	1.794	1.777	1.776	1.799	1.810	1.816
$\angle CINC1$	111.1	110.8	110.2	110.3	110.1	109.9	132.8	131.9	131.5	131.4	131.3	131.1	85.4	85.9	85.0	85.6	85.5	84.2
ΔE^b	0.0	0.0	0.0	0.0	0.0	0.0	2.188	2.270	2.308	2.326	2.364	2.353	3.606	3.282	3.010	3.148	3.097	3.024
μ	0.5954	0.6755					0.3103	0.4066					1.3519	1.5502				
q_N	-0.07	-0.27					-0.26	-0.27					-0.25	-0.31				
S_{N-Cl}	0.275	0.236					0.191	0.162					0.092	0.057				
BE ^c	19.7	49.2	102.1	82.4	91.9	99.6	-30.7	-3.2	25.2	28.8	37.3	45.4	-63.4	-26.5	32.7	9.8	20.4	29.9

	\tilde{C}^2A_1						\tilde{D}^2A_2					
	SCF	CISD	MP2	CI-Q ^a	F-CI ^a	MP4	SCF	CISD	MP2	CI-Q ^a	F-CI ^a	MP4
R_{N-Cl}	1.826	1.804	1.757	1.818	1.827	1.791	1.814	1.797	1.794	1.819	1.832	1.838
$\angle CINC1$	136.7	134.2	129.2	133.2	132.4	128.7	98.5	99.7	101.0	99.6	99.7	100.7
ΔE	4.197	3.746	3.325	3.396	3.240	2.967	5.044	4.563	4.101	4.291	4.172	4.007
μ	0.1495	0.0486					1.3382	1.5372				
q_N	+0.17	+0.09					-0.26	-0.33				
S_{N-Cl}	-0.181	-0.255					0.054	0.024				
BE ^c	-77.0	-37.2	25.4	4.1	17.1	31.2	-96.9	-56.0	7.50	-16.5	-4.4	7.2

^a Correction for the unlinked quadruples (CI-Q) and full-CI (F-CI) extrapolation according to Davidson's formulas³¹. ^b Ground state energy values (E_h): $E_{SCF} = -973.38878$, $E_{CISD} = -973.91212$, $E_{CI-Q} = -973.9944$, $E_{F-CI} = -974.0115$, $E_{MP2} = -973.95044$, $E_{MP4} = -974.01637$. ^c BE = $E(NCl_2; \text{state}) - E(N; ^4S) - 2E(Cl; ^2P)$. Negative values mean unbound states always with respect to ground state fragments.

TABLE 2: Bond Distances R_e (Å), Bond Angles (deg), Energy Differences ΔE (eV) with Respect to the Ground State, Dipole Moments μ (D), Net Mulliken Charges q , Overlaps S , and Binding Energies BE (kcalmol⁻¹) of the PCl₂ Molecule in the Ground \tilde{X}^2B_1 and Low-Lying States and in Different Methodologies

	\tilde{X}^2B_1						\tilde{A}^2A_1						\tilde{B}^2B_2					
	SCF	CISD	MP2	CI-Q ^a	F-CI ^a	MP4	SCF	CISD	MP2 ^d	CI-Q ^a	F-CI ^a	MP4 ^d	SCF	CISD	MP2 ^d	CI-Q ^a	F-CI ^a	MP4 ^d
R_{P-Cl}	2.054	2.044	2.044	2.052	2.057	2.055	2.161	2.140		2.145	2.150		2.145	2.146		2.158	2.164	
$\angle CIPC1$	102.1	101.7	101.7	101.9	101.9	101.8	152.8	153.9		153.1	153.6		87.1	88.5		88.4	88.4	
ΔE^b	0.0	0.0	0.0	0.0	0.0	0.0	2.676	2.528		2.384	2.327		3.588	3.396		3.249	3.192	
μ	0.9798	0.8129					0.6614	0.4852					1.9895	1.6916				
q_P	+0.09	+0.07					+0.14	+0.12					+0.10	+0.08				
S_{P-Cl}	0.426	0.400					0.098	0.066					0.114	0.081				
BE ^c	90.0	96.7	146.7	125.3	134.0	141.1	28.3	38.4		70.3	80.3		7.22	18.4		50.3	60.4	

	\tilde{C}^2A_1						\tilde{D}^2B_2						\tilde{E}^2A_2					
	SCF	CISD	MP2	CI-Q ^a	F-CI ^a	MP4	SCF	CISD	MP2	CI-Q ^a	F-CI ^a	MP4	SCF	CISD	MP2 ^d	CI-Q ^a	F-CI ^a	MP4 ^d
R_{P-Cl}	2.024	2.031	2.024	2.040	2.046	2.043	2.211	2.195	2.183	2.204	2.210	2.204	2.229	2.212		2.218	2.223	
$\angle CIPC1$	120.0	120.0	120.0	118.6	118.1	120.1	71.1	71.4	70.8	71.7	71.9	71.0	85.4	86.3		87.4	88.5	
ΔE	3.816	3.683	3.589	3.572	3.532	3.502	4.142	3.905	3.783	3.731	3.663	3.657	5.473	5.105		4.795	4.664	
μ	0.3167	0.2073					0.1244	0.3756					0.3052	0.5800				
q_P	+0.02	+0.02					0.01	0.00					+0.01	-0.02				
S_{P-Cl}	0.358	0.325					0.154	0.138					0.123	0.113				
BE ^c	1.96	11.8	63.9	42.9	52.5	60.4	-5.5	6.7	59.5	39.2	49.5	56.8	-36.2	-21.0		14.7	26.4	

^a Correction for the unlinked quadruples (CI-Q) and full-CI (F-CI) extrapolation according to Davidson's formulas³¹. ^b Ground state energy values (E_h): $E_{SCF} = -1259.81933$, $E_{CISD} = -1260.29084$, $E_{CI-Q} = -1260.3703$, $E_{F-CI} = -1260.3865$, $E_{MP2} = -1260.32394$, $E_{MP4} = -1260.38880$. ^c BE = $E(PCl_2; \text{state}) - E(P; ^4S) - 2E(Cl; ^2P)$. Negative values mean unbound states always with respect to the ground state fragments. ^d We were unable to obtain MP2 and MP4 results for purely technical reasons.

$$T(v, J) = D_e + \omega_e(v + 1/2) + B_e J(J + 1) - \omega_e x_e (v + 1/2)^2 + \alpha_e (v + 1/2) J(J + 1) + \bar{D}_e J^2 (J + 1)^2 + Y_{00}$$

The constant Y_{00} , being in all cases a fraction of a wave number, is not listed in Table 5.

We would like first to make some general comments focusing on the ground, \tilde{X}^2B_1 , and $X^3\Sigma^-$ symmetries; our conclusions apply more or less to the excited states as well. As is evidenced from Tables 1–4, CISD and MP2 geometries are very similar; the same is true for the F-CI and MP4 geometries. The MP2 binding energies (BE) are rather overestimated, being the highest in comparison with values obtained via the other techniques. Again, F-CI and MP4 BE values are in reasonable agreement with each other, the MP4 values being always larger by no more than 8%. As expected, the CISD BE values are underestimated, as can be judged from the experimental dissociation energies of NCl³³ and PCl³⁴ molecules (Tables 3–5). It is interesting

to note that the MP2 D value of PCl is in good agreement with the experimental number³⁴ (Tables 4 and 5), a rather fortuitous result.

We examine now every molecular species separately, starting from NCl₂. Experimental geometrical data are virtually unknown for NCl₂. From matrix infrared spectra,³⁵ the CINC1 angle has been deduced to be $111 \pm 4^\circ$, in agreement with our theoretical predictions (Table 1) for the state \tilde{X}^2B_1 . Also, the DFT structural results of Austen et al.⁵ for the \tilde{X}^2B_1 state coincide with our CISD (or essentially SCF) numbers. From Table 1 and with the exception of the \tilde{C}^2A_1 state, we observe that going from SCF to MP4 the N–Cl bond length increases almost monotonically. For the two most reliably calculated states, i.e., \tilde{X}^2B_1 and \tilde{A}^2A_1 , and in all post-HF methods used, the CINC1 angle does not vary by more than 0.9° , but the precision is certainly lower for the N–Cl bond length, the largest difference being 0.022 \AA (\tilde{X}^2B_1 , CISD vs MP4).

TABLE 3: Bond Distances R_e (Å), Bond Angles (deg), Energy Differences ΔE (eV) with Respect to the Ground State, Dipole Moments μ (D), Net Mulliken Charges q , Overlaps S , and Dissociation Energies D_e (kcalmol⁻¹) of the NCl Molecule in the $X^3\Sigma^-$, $a^1\Delta$, and $b^1\Sigma^+$ States, As Obtained by SCF and CISD Methods

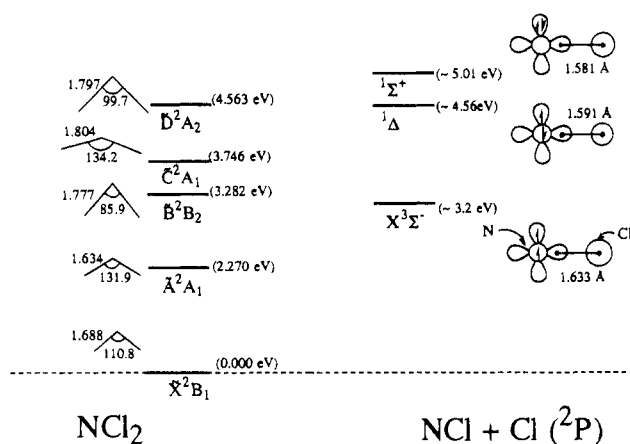
	$X^3\Sigma^-$ ^a							$a^1\Delta$					$b^1\Sigma^+$				
	SCF	CISD	CI-Q ^b	F-Cl ^b	MP2	MP4	exp	SCF	CISD	CI-Q ^b	F-Cl ^b	exp	SCF	CISD	CI-Q ^b	F-Cl ^b	exp
R_{N-Cl}	1.655	1.633	1.635	1.635	1.622	1.636	1.6107 ^e	1.621	1.591	1.598	1.598		1.586	1.581	1.595	1.598	1.5713 ^h
ΔE^c	0.0	0.0	0.0	0.0	0.0	0.0		1.606	1.356	1.303	1.292	1.150 ^g	2.281	1.812	1.694	1.665	1.858 ^h
μ	0.4466	0.8026						0.8542	1.3097				1.2338	1.5080			
q_N	-0.027	-0.081						-0.09	-0.17				-0.15	-0.20			
S_{N-Cl}	0.261	0.243						0.287	0.261				0.318	0.275			
D_e^d	12.3	37.6	52.3	55.0	56.6	56.3	80±2 ^f	-24.7	6.3	22.2	25.2		-40.3	-4.2	13.2	16.0	

^a For the $X^3\Sigma^-$ state only, MP2 and MP4 values are also listed. ^{b,d} See Table 1 or 2. ^c Ground state energy values (E_n): $E_{SCF} = -513.896$ 97, $E_{CISD} = -514.231$ 89, $E_{CI-Q} = -514.2732$, $E_{F-Cl} = -514.2787$, $E_{MP2} = -514.232$ 82, $E_{MP4} = -514.275$ 50. ^e Reference 15. ^f Reference 33. ^g Reference 43. ^h Reference 39.

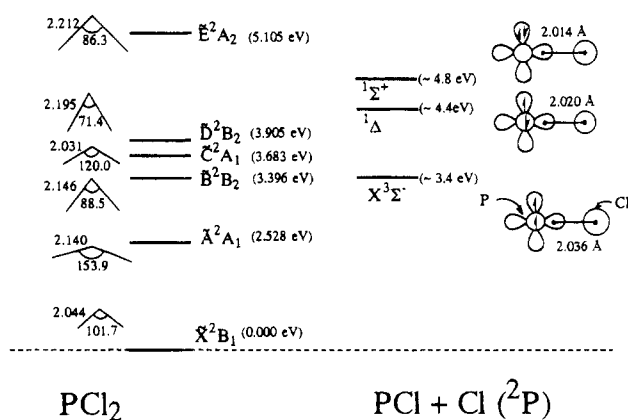
TABLE 4: Bond Distances R_e (Å), Bond Angles (deg), Energy Differences ΔE (eV) with Respect to the Ground State, Dipole Moments μ (D), Net Mulliken Charges q , Overlaps S , and Dissociation Energies D_e (kcalmol⁻¹) of the PCl Molecule in the $X^3\Sigma^-$, $a^1\Delta$, and $b^1\Sigma^+$ States, As Obtained by SCF and CISD Methods

	$X^3\Sigma^-$ ^a							$a^1\Delta$				$b^1\Sigma^+$				
	SCF	CISD	CI-Q ^b	F-Cl ^b	MP2	MP4	exp	SCF	CISD	CI-Q ^b	F-Cl ^b	SCF	CISD	CI-Q ^b	F-Cl ^b	exp
R_{P-Cl}	2.046	2.036	2.042	2.045	2.031	2.042	2.0146 ^e	2.031	2.020	2.026	2.029	2.018	2.014	2.023	2.024	
ΔE^c	0.0	0.0	0.0	0.0	0.0	0.0		1.114	0.960	0.920	0.906	1.689	1.383	1.265	1.230	1.499 ^g
μ	1.0578	0.7965						0.8234	0.5384			0.6102	0.3879			
q_P	+0.19	+0.14						+0.16	+0.10			+0.13	+0.08			
S_{P-Cl}	0.343	0.335						0.348	0.341			0.356	0.348			
D_e^d	43.6	52.8	64.3	66.8	71.7	69.3	78.9±9.5 ^g	17.9	30.6	43.1	45.9	4.7	20.9	35.2	38.5	

^a For the $X^3\Sigma^-$ state only, MP2 and MP4 values are also listed. ^{b,d} See Table 1 or 2. ^c Ground state energy values (E_n): $E_{SCF} = -800.263$ 79, $E_{CISD} = -800.562$ 14, $E_{CI-Q} = -800.6000$, $E_{F-Cl} = -800.6054$, $E_{MP2} = -800.559$ 33, $E_{MP4} = -800.602$ 70. ^e Reference 16. ^f Reference 39. ^g Reference 34.

**Figure 1.** Manifold of spectroscopic states for NCl_2 and $NCl + Cl(^2P)$ calculated at the CISD level. Bond lengths in Å, angles in deg.

Gilbert et al.³⁶ observed the photolysis of nitrogen trichloride, NCl_3 . The spectrum of the emission for the 248 nm (5.00 eV) excitation of NCl_3 consists of unresolved emission from 476 to 744 nm (2.61 to 1.67 eV) with a maximum at 546 nm (2.271 eV).³⁶ They assigned this 2.271 eV unresolved emission to an unknown state of the photoproduct NCl_2 (Figure 6 of ref 34). We propose that this is the \tilde{A}^2A_1 state of NCl_2 ; Table 1 and Figure 1 show that the calculated energy gap $\Delta E_{\tilde{A}^2A_1-\tilde{X}^2B_1}$ at the CISD (or MP4) level is in very good agreement with the experimental results. Recently, Gilbert and Hofsetz³⁷ observed the UV absorption spectrum of NCl_2 in a low-temperature argon matrix. The spectrum consists of diffuse bands, possibly overlying a continuum, and extends from 270 to 320 nm (4.59 to 3.87 eV), with a maximum at about 295 nm (4.20 eV) (Figure 2 of ref 35). They deduced that this is not a transition to the lowest lying electronic state of NCl_2 . Their inferences seem to be confirmed by our calculations. Table 1 (see also Figure 1) suggests that the excited state involved is of \tilde{D}^2A_2 symmetry, $\Delta E_{\tilde{D}^2A_2-\tilde{X}^2B_1} \approx 4.0-4.6$ eV depending on the method of

**Figure 2.** Manifold of spectroscopic states for PCl_2 and $PCl + Cl(^2P)$ calculated at the CISD level. Bond lengths in Å, angles in deg.

calculation. The state \tilde{B}^2B_2 of Table 1 can be ruled out as a possible candidate for two reasons: it is energetically very low, and it is also dipole forbidden by symmetry. State \tilde{C}^2A_1 can also be excluded due to its low energy. Finally, the diffuse band structure of the UV absorption spectrum³⁷ is indicative of a predissociated state. Therefore, NCl_2 is expected to fragment under UV irradiation to NCl and Cl . Our theoretical results clearly corroborate the experimental conclusions, the \tilde{D}^2A_2 state of NCl_2 being much higher than the energies of $NCl(^3\Sigma^-) + Cl(^2P)$ (Figure 1).

We turn now to the PCl_2 species. Table 2 and Figure 2 summarize our findings on this system. For the \tilde{X}^2B_1 state the LDA geometrical results of Austen et al.⁵, $R_{P-Cl} = 2.041$ Å, $\angle CIPCl = 102.1^\circ$, are very close to our CISD predictions (Table 2). Gutsev¹⁰ at the LSDA level reports the following geometrical results for the \tilde{X}^2B_1 and 2A_1 states of PCl_2 : $R_{P-Cl} = 2.065$ Å, $\angle CIPCl = 102.6^\circ$ (\tilde{X}^2B_1) and $R_{P-Cl} = 2.041$ Å, $\angle CIPCl = 121^\circ$ (2A_1), with $\Delta E_{^2A_1-\tilde{X}^2B_1} = 3.41$ eV. The LSDA bond length of the \tilde{X}^2B_1 state is larger than ours by 0.01–0.02 Å, depending on the method employed, while the bond angle

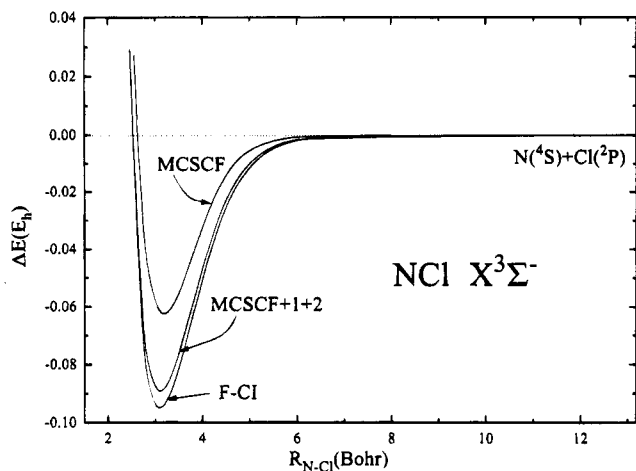


Figure 3. Energy potential curve of the X³Σ⁻ state of the NCl radical at the MCSCF, MCSCF+1+2, and F-CI levels.

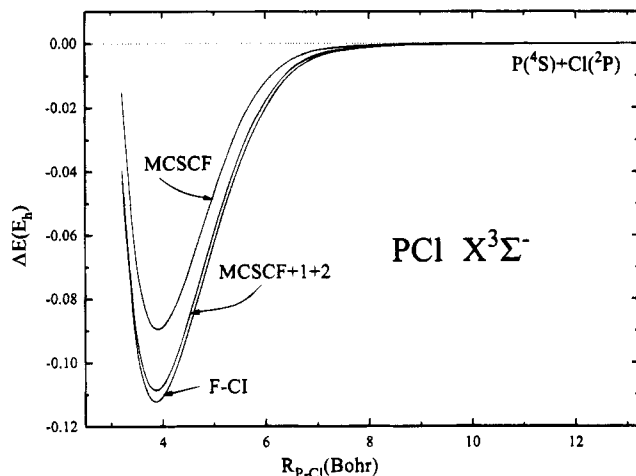


Figure 4. Energy potential curve of the X³Σ⁻ state of the PCl radical at the MCSCF, MCSCF+1+2, and F-CI levels.

TABLE 5: Absolute Energies *E* (hartree), Dissociation Energies *D*₀ (kcal·mol⁻¹), Bond Lengths *R*_e (Å), and Spectroscopic Constants (cm⁻¹) of the NCl and PCl Molecules in Their X³Σ⁻ State

method	- <i>E</i>	<i>D</i> ₀ ^a	<i>R</i> _e	<i>ω</i> _e ^b	<i>ω</i> _e <i>χ</i> _e ^c	<i>α</i> _e ^d	<i>D</i> _e ^e
NCl							
MCSCF	513.93973	38.1	1.686	723.3	5.75	6.37	1.60
MCSCF+1+2	514.25094	54.8	1.643	798.0	5.46	6.29	1.53
F-CI ^f	514.2879	58.5	1.638	809.8	5.20	6.26	1.51
exp		80±2 ^g	1.6107 ^h	828.0 ^h	5.30 ^h	6.41 ^h	1.60 ^h
PCl							
MCSCF	800.28554	55.4	2.069	513.8	2.27	1.50	0.21
MCSCF+1+2	800.57269	67.4	2.046	539.2	2.42	1.56	0.20
F-CI ^f	800.6129	69.6	2.046	537.4	2.30	1.51	0.20
exp		78.9±9.5 ⁱ	2.0146 ^j	551.4 ^j	2.23 ^j	1.51 ^j	0.21 ^j

^a *D*₀ = *D*_e - *ω*_e/2. ^b Harmonic frequency. ^c First anharmonic constant. ^d Rotation-vibration coupling constant. ^e Centrifugal distortion. ^f See Table 1 or 2. ^g Reference 33. ^h Reference 15. ⁱ Reference 34. ^j Reference 17.

is larger by 1° independent of the method of computation (Table 2). The ²A₁ state of Gutsev¹⁰ corresponds to the \tilde{C}^2A_1 state of Table 2 (see previous section). The LSDA geometrical results for this state are quite similar to our CISD or MP4 numbers, while the LSDA excitation energy $\Delta E_{\tilde{A}^2A_1-\tilde{X}^2B_1}$ does not differ by more than 0.3 eV (CISD) in any correlated method reported in Table 2. The MP2/6-31G* structural results by Brum and Hudgens⁹ for the \tilde{X}^2B_1 state are practically the same as the MP2 results of Table 2, with the difference in total energy of -0.2455

hartree being entirely due to the superior basis set used in the present study.

Bramwell et al.⁸ observed the 193 nm (6.42 eV) photolysis of PCl₃ and a concomitant emission peaking at approximately 460 nm (2.70 eV) and attributed it to the PCl₂ radical, $\Delta E_{\tilde{A}^2A_1-\tilde{X}^2B_1}$. We have calculated a $\Delta E_{\tilde{A}^2A_1-\tilde{X}^2B_1} \approx 2.5$ eV at the CISD level (Table 2, Figure 2), thus confirming the experimental findings, clarifying at the same time which of the two ²A₁ states is involved in the observed emission. Notice the very large structural differences between the \tilde{A}^2A_1 and \tilde{C}^2A_1 states and, in particular, between the \tilde{X}^2B_1 and \tilde{A}^2A_1 states.

NCl. Table 3 presents our results on NCl for the states X³Σ⁻, a¹Δ, and b¹Σ⁺ in different methodologies. Table 5 lists results on the ground X³Σ⁻ state only at the MCSCF, MCSCF+1+2, and F-CI levels of theory along with experimental findings, while Figure 3 shows the corresponding complete potential energy curves.

At the MRDCI/DZ+P level, Bettendorff and Peyerimhoff¹⁹ predict the following N-Cl bond lengths and excitation energies for the three states mentioned above: 1.647 (X³Σ⁻), 1.610 (Δ), and 1.599 (Σ⁺) Å; $\Delta E_{\Delta-X^3\Sigma^-} = 1.32$ eV and $\Delta E_{b^1\Sigma^+-X^3\Sigma^-} = 2.08$ eV. From Table 3 we observe, on average and in all post-HF methods employed, that our results are in better agreement with the experimental values than the results of ref 19. However, all methods listed in Table 3 fail to predict a reasonable ground state dissociation energy, our best number being 30% lower than the experimental value.³³ In particular, the SCF value is approximately one seventh of the experimental one, indicating the difficulty of obtaining this quantity correctly. At the MRDCI+corrections level Bettendorff and Peyerimhoff¹⁹ predict a N-Cl(X³Σ⁻) *D*_e = 63.4 kcal·mol⁻¹. With the problem of the NCl *D*_e in mind we decided to carry out some larger calculations, and the results are shown in Table 5.

At the MCSCF level we observe a significant improvement of the *D*_e value (*D*_e = *D*₀ + *ω*_e/2 = 39.1 kcal·mol⁻¹) of the X³Σ⁻ state over the SCF value (Table 3), while at the same time the bond length increases markedly as compared to the SCF value, rendering the comparison with experiment worse. The extrapolated to the F-CI MCSCF+1+2 results, although improved, are not satisfactory, the *D*₀ value being 73% of the experimental and the bond length being 0.027 longer than the observed.¹⁵ On the contrary, the spectroscopic MCSCF+1+2 (and F-CI) constants, namely *ω*_e, *ω*_e*χ*_e, *α*_e, and \bar{D}_e are in very good agreement with the experimental results.¹⁵ In an interesting, very recent article by Simons and co-workers³⁸ concerning theoretical results on the 120 first- and second-row diatomic molecules, a theoretical *D*_e value of 58.1 kcal·mol⁻¹ extracted from the literature is reported for the NCl(X³Σ⁻) species, a number almost identical to the one reported in Table 5. Lievin and Metz¹⁸ at the MCSCF+correlation level for the X³Σ⁻ state report a *D*_e = 49.3 kcal·mol⁻¹ and a *R*_{N-Cl} = 1.651 Å, with corresponding values at the MCSCF level of 26.5 kcal·mol⁻¹ and 1.744 Å, respectively.

At this point we would like only to emphasize that NCl is a difficult and fastidious molecular system. As was mentioned earlier, only the MP4SDQ bond length of Peterson and Woods²⁰ reproduces the experimental value within 0.01 Å, *R*_{N-Cl} = 1.6192 Å. Yet, these workers report a *D*_e = 58.1 kcal·mol⁻¹ as compared to 58.5 + *ω*_e/2 = 59.7 kcal·mol⁻¹ reported in Table 5 at the extrapolated MCSCF+1+2 level. It is interesting to note that the CISD and MP4SDQ total energies given in ref 20 are ~3 and 10 mhartrees lower and higher than our CISD and MP4SDTQ energies, respectively.

PCl. Table 4 presents our results in different methodologies on PCl for the states X³Σ⁻, a¹Δ, and b¹Σ⁺. The second part of

Table 5 lists results on the $X^3\Sigma^-$ state only, at the MCSCF, MCSCF+1+2, and F-CI levels of theory, along with experimental results, while Figure 4 shows the corresponding complete potential energy curves.

At the MP2/6-31G* level Nguyen²¹ reports the bond distances 2.037 ($X^3\Sigma^-$) and 2.014 ($b^1\Sigma^+$) Å, in complete agreement with the CISD results of Table 4. The $\Delta E = 1.36$ eV MP4SDTQ/6-31G*/MP2 value reported in ref 21 is also in agreement with our CISD value given in Table 4. Large energy differences of the absolute energies between the present and Nguyen's²¹ work, 140–180 mhartrees, are entirely due to the superior basis set used here.

For the $X^3\Sigma^-$ state Gutsev¹⁰ reports a bond length of 2.047 Å and a $D_e = 91.5$ kcal·mol⁻¹ at the LSDA level and a $D_e = 71.5$ kcal·mol⁻¹ at the LSDA/NL (LSDA+nonlocal gradient correction of the exchange term) level. The LSDA bond length and the LSDA/NL D_e 's are comparable with the corresponding MP4 values (Table 4).

Now a few things are clear from Table 4: The P–Cl bond length in all three states, $X^3\Sigma^-$, $a^1\Delta$, and $b^1\Sigma^+$, is not sensitive to the method of computation. At the SCF level the binding energy is already 55% of the experimental, in marked contrast with the case of NCl (Table 3), and the final D_0 value at the extrapolated MCSCF+1+2 level can be considered in fair agreement with the experimental³⁴ value (Table 5). At the MCSCF+1+2 (or F-CI) level the spectroscopic constants ω_e , $\omega_e x_e$, α_e , and \bar{D}_e are in respectable agreement with the experimental¹⁷ values, yet the bond distance is by 0.03 Å larger than the experimental¹⁷ value. From Tables 4 and 5 we can see that the MP4 and the MCSCF+1+2 D_e and R_e values of the $X^3\Sigma^-$ state of PCl are practically the same.

Concluding Remarks

(a) The triatomic species NCl₂ and PCl₂ have a bent ground state of 2B_1 symmetry and can be clearly characterized as π -radicals with the symmetry-carrying electron perpendicular to the plane of the molecule. The same holds true for the corresponding isovalent species NH₂,⁴⁰ NF₂,¹ and PH₂,⁴⁰ PF₂.^{41,42} Notice that the range of the ground state bond angles in the NX₂ and PX₂ series (X = H, F, Cl) is about 7° and 10°, respectively, with the smallest angles being 104° (NH₂) and 91.5° (PH₂).

(b) Although for both NCl₂ and PCl₂ species the first excited state is of 2A_1 symmetry, the electronic configuration of the former is of an entirely different nature from the configuration of the latter (*vide supra*).

(c) The energy gap $\Delta E_{\tilde{X}^2B_1-\tilde{A}^2A_1}$ for both NCl₂ and PCl₂ molecules is about the same, 2.3–2.5 eV, while the analogous energy difference in NF₂¹ (or PF₂⁴²) is ~4.5 eV. The electronegativity difference $\Delta\chi^P$ (Pauling's scale) between N and F and P and Cl is 1.0 and 0.7, respectively, with the positive charge on the N and P atoms. The population analysis (Tables 1 and 2) confirms the electronegativity predictions. Taking into account that the first excited state of PCl₂(\tilde{A}^2A_1) is of a different nature than either the NCl₂ or NF₂ \tilde{A}^2A_1 state (*vide supra*), we see a consistent behavior between electronegativity differences and energy gaps. In NCl₂ the situation is totally different because the N atom is strongly negatively charged. The fact that the first excited states of NCl₂ and PCl₂ both lie 2.3–2.5 eV above the ground state is rather fortuitous.

(d) In the NCl($X^3\Sigma^-$) system the MCSCF+1+2 (or F-CI) calculation seems to fail to predict accurately enough either the dissociation energy D_0 or the bond length, yet the rest of the calculated spectroscopic constants are in excellent agreement with the experimental results (Table 5). However, all high-

level calculations in the literature,^{19,20,38} the present included, converge to a dissociation energy D_e less than 65 kcal·mol⁻¹. Although definitely we need a larger basis set and possible diffuse functions in order to obtain a trusted D_0 value, we believe that the experimental dissociation energy,³³ 80 ± 2 kcal·mol⁻¹, is too large. Benchmark calculations for the molecule, using a series of basis sets of increasing size, are already in progress.⁴⁴ The situation is better for the PCl species, but here also the basis set size appears to be the problem for the much larger bond length compared to the experimental number (Table 5).

(e) We would like to point out that for almost all states and for all four species the SCF bond lengths are larger than the corresponding CISD bond lengths, which is against the conventional wisdom of these methodologies.

(f) Finally, although in NF₂ radical photolysis to NF($^1\Delta$ or $X^3\Sigma^-$)+F(2P) can occur from the first excited \tilde{A}^2A_1 state located 4.5 eV above the ground \tilde{X}^2B_1 state,¹ an analogous photolytic process for the NCl₂ and PCl₂ species cannot happen, because the \tilde{A}^2A_1 state is lower than the $X^3\Sigma^-$ state (Figures 1 and 2).

Acknowledgment. The financial support of the (Greek) General Secretariat of Research and Technology that made this work possible (Grant No. 91 EΔ113) is greatly appreciated. We also appreciate the general help of the Supercomputer Center of the NCSR DEMOKRITOS (Greece). One of us (A.M.) is an adjunct member of the Physical Chemistry Institute of NCSR DEMOKRITOS.

References and Notes

- (1) Papakondylis, A.; Mavridis, A. *Chem. Phys. Lett.* **1993**, *216*, 167.
- (2) Briggs, A. G.; Norrish, R. G. W. *Proc. R. Soc. London* **1964**, *278*, 27.
- (3) Gilbert, J. V.; Brendon, H. D. *J. Phys. Chem.* **1992**, *96*, 4321 and references therein.
- (4) Hincheliffe, A.; Bounds, D. G. *J. Mol. Struct.* **1979**, *54*, 231.
- (5) Austen, M. A.; Eriksson, L. A.; Boyd, R. J. *Can. J. Chem.* **1994**, *72*, 695.
- (6) Kharasch, M. S.; Jansen, E. V.; Urry, W. H. *J. Am. Chem. Soc.* **1945**, *67*, 1864.
- (7) Andrews, L.; Frederick, D. L. *J. Phys. Chem.* **1969**, *73*, 2774.
- (8) Bramwell, M. J.; Jaeger, S. E.; Whitehead, J. C. *Chem. Phys. Lett.* **1992**, *196*, 547 and references therein.
- (9) Brum, J. L.; Hudgens, J. W. *J. Phys. Chem.* **1994**, *98*, 5587.
- (10) Gutsev, G. L. *Chem. Phys.* **1994**, *179*, 325.
- (11) Gilbert, J. V.; Smith, L. J. *J. Phys. Chem.* **1991**, *95*, 7278.
- (12) Ray, A. J.; Coombe, R. D. *J. Phys. Chem.* **1993**, *97*, 3475 and references therein.
- (13) Yamada, C.; Endo, Y.; Hirota, E. *J. Chem. Phys.* **1983**, *79*, 4159.
- (14) Yamada, C.; Endo, Y.; Hirota, E. *J. Mol. Spectrosc.* **1986**, *115*, 105.
- (15) Yamada, C.; Endo, Y.; Hirota, E. *J. Mol. Spectrosc.* **1986**, *117*, 134.
- (16) Minowa, T.; Saito, S.; Hirota, E. *J. Chem. Phys.* **1985**, *83*, 4939.
- (17) Kanamori, H.; Yamada, C.; Butler, J. E.; Kawaguchi, K.; Hirota, E. *J. Chem. Phys.* **1985**, *83*, 4945.
- (18) Lievin, J.; Metz, J.-Y. *Theor. Chim. Acta* (Berlin) **1985**, *67*, 391.
- (19) Bettendorff, M.; Peyerimhoff, S. D. *Chem. Phys.* **1986**, *104*, 29.
- (20) Peterson, K. A.; Woods, R. C. *J. Chem. Phys.* **1990**, *93*, 1876.
- (21) Nguyen, M. T. *Mol. Phys.* **1986**, *59*, 547.
- (22) Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Chem. Phys.* **1991**, *94*, 7221.
- (23) Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007.
- (24) Woon, D. E.; Dunning, T. H., Jr. *J. Chem. Phys.* **1993**, *98*, 1358.
- (25) Raffanetti, R. J. *J. Chem. Phys.* **1973**, *58*, 4458.
- (26) Davidson, E. R. *MELD*; Department of Chemistry, Indiana University, Bloomington, IN.
- (27) GAUSSIAN series of programs: Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Pople, J. A. *Gaussian 92*, Revision B; Gaussian, Inc.: Pittsburgh, PA, 1992.
- (28) Shepard, I. R.; Shavit, I.; Pitzer, R. M.; Comeau, D. C.; Pepper, M.; Lischka, H.; Szalay, P. G.; Ahlrichs, R.; Brown, F. B.; Zhao, I. G. *Int. J. Quantum Chem.* **1988**, *322*, 149.
- (29) Bartlett, R. J. *Annu. Rev. Phys. Chem.* **1981**, *32*, 359.

- (30) Duch, W.; Diercksen, G. H. F. *J. Chem. Phys.* **1994**, *101*, 3018.
- (31) Davidson, E. R.; Silver, D. W. *Chem. Phys. Lett.* **1977**, *52*, 403.
- (32) See for instance: Levine, I. N. *Quantum Chemistry, Vol II. Molecular Spectroscopy*; Allyn and Bacon: Boston, 1970.
- (33) Clark, T. C.; Clyne, M. A. A. *Trans. Faraday Soc.* **1970**, *66*, 877.
- (34) *Thermodynamical Properties of Individual Compounds*; Glushko, V. P., Ed.; Nauka: Moscow, 1979 (as listed in ref 10).
- (35) Kohlmitter, C. K.; Andrews, L. *Inorg. Chem.* **1982**, *21*, 1519.
- (36) Gilbert, J. V.; Wu, X. L.; Stedman, D. H.; Coombe, R. D. *J. Phys. Chem.* **1987**, *91*, 4265.
- (37) Gilbert, J. V.; Hofsetz, B. D. *J. Phys. Chem.* **1992**, *96*, 4321.
- (38) Boldyrev, A. I.; Gonzales, N.; Simons, J. *J. Phys. Chem.* **1994**, *98*, 9931 and references therein. In this paper an experimental $D = 4.8$ eV ($=110.7$ kcal·mol⁻¹) value is reported referring to the book by Huber and Herzberg.³⁹ Such a value does not exist in the H. H. book; as a matter of fact the corresponding entry is empty.
- (39) Huber, K. P.; Herzberg, G. *Molecular Spectra and Molecular Structure, Constants of Diatomic Molecule*; van Nostrand Reinhold: New York, 1979.
- (40) Herzberg, G. *Electronic Spectra and Electronic Structure of Polyatomic Molecules, Molecular Spectra and Molecular Structure*; van Nostrand: New York, 1966.
- (41) Saito, S.; Endo, Y.; Hirota, E. *J. Chem. Phys.* **1986**, *85*, 1778.
- (42) Glezakou, V. A.; Kapellos, S. T.; Mavridis, A. *THEOCHEM* **1994**, *305*, 225.
- (43) Pritt, A. T.; Patel, D., Jr.; Coombe, R. D. *J. Mol. Spectrosc.* **1981**, *87*, 401.
- (44) Xantheas, S. S.; Dunning, T. H., Jr.; Papakondylis, A.; Mavridis, A. To be published.

JP950323V