



ELSEVIER

International Journal of Mass Spectrometry 201 (2000) 269–275



Heat of formation of the CF_2^{++} dication: a theoretical estimate

Jan Hrušák^{a,*}, Zdenek Herman^a, Nadja Sändig^b, Wolfram Koch^b

^a*J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, Dolejškova 3, CZ 18223 Prague 8, Czech Republic*

^b*Institut für Organische Chemie der Technischen Universität Berlin, Straße des 17. Juni 135, D-10623 Berlin, Germany*

Received 29 October 1999; accepted 31 January 2000

Abstract

Relative energies and ionization potentials of neutral and ionic fragments of CF_4 were calculated using the coupled cluster single double (triple)/correlation consistent triple zeta basis set *ab initio* method. The individual values were compared with available experimental and theoretical data to assess the accuracy of this approach for these particular systems. In addition, reaction enthalpies for possible fragmentation reactions were calculated. Maximum errors found were in the order of 5 kcal/mol (0.2 eV). The estimation of the heat of formation of the CF_2^{++} dication, derived from the calculations based on four different reactions, is 687 ± 5 kcal/mol (29.8 ± 0.2 eV). This value is considerably smaller than the one which follows from the appearance potential measurements (732 ± 7 kcal/mol). (Int J Mass Spectrom 201 (2000) 269–275) © 2000 Elsevier Science B.V.

Keywords: Dication; CF_2^{++} ; Coupled cluster

1. Introduction

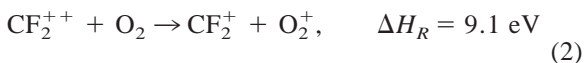
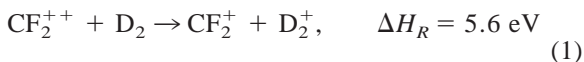
Long-lived polyatomic dications have attracted considerable attention of both experimentalists [1,2] and theoreticians [3,4] during the past two decades. These dications sometimes exhibit unusual structures and reactivities and in this context they represent a challenging topic in gas phase ion chemistry. The CF_n^+ and CF_n^{++} series of cations and dications are of particular interest, e.g. due to their importance in plasma etching processes [5,6]. Furthermore, it is believed that CF_n^{x+} ions play a key role in the depletion of ozone in the outer atmosphere [7].

The thermochemistry of various decomposition

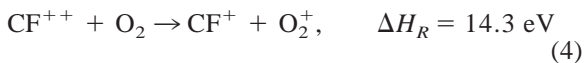
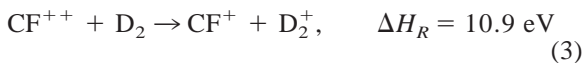
products of CF_4 is of importance in evaluating and modeling the reactions that involve these species. Unfortunately, thermochemical values of some species show a large scatter [8] and, in particular, limited information is available on dications. The first measurements of appearance energies (AE) of doubly charged fragment ions of CF_4 led to 42.7 ± 0.3 eV for CF_3^{++} and 44.3 ± 0.3 eV for CF_2^{++} [9]. More recent measurements [10] gave 41.8 ± 0.3 eV for CF_3^{++} , 42.9 ± 0.3 eV for CF_2^{++} , and, in addition, 52.1 ± 0.3 eV for CF^{++} . Beynon and co-workers [11] determined the ionization energies (IEs) of the singly charged ions, 26.0 ± 0.4 eV for CF^+ and 26.3 ± 0.4 eV for CF_3^+ , by a direct Q_{\min} measurement using the charge stripping technique, and they also observed the presence of long lived excited states of the cations. Unfortunately, due to the low instru-

* Corresponding author. E-mail: hrusak@jh-inst.cas.cz

ment resolution and interference of the $C_4H_2^{++}$ ion (m/z 50), the corresponding measurements to identify the $IE(CF_2^+)$ failed. Later on, the reactivity of CF_2^{++} and CF_3^{++} dications was studied by Leone and co-workers [12–14] in collision experiments with a series of gases. From studies of charge transfer reactions with rare gases and skillful application of the reaction window concept, the double ionization energy $IE_1^{--}(CF_2)$ was estimated to be between 32.0 and 33.0 eV [13]. Using these values and the most recent IE of difluorocarbene (CF_2), 11.445 eV [8], $IE(CF_2^+)$ should be between 20.5 and 21.5 eV. From their subsequent article [14] an IE for CF_2^+ of 21.1 eV can be derived. In these calculations we use $IE(O_2) = 12.07$ eV and $IE(D_2) = 15.47$ eV [8] as well as the reported exothermicities of the reactions

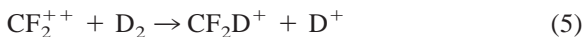


The occurrence of an excited state of CF_2^{++} lying ~ 4.0 eV above the lower state is also mentioned in that article. Similarly, a value of 26.4 eV for $IE(CF^+)$ can be obtained from the exothermicities of the following reactions:



These data are in perfect agreement with the value given by Beynon and co-workers already in 1982 [11].

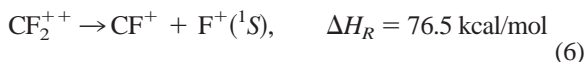
Recently, dynamics of reaction (1) have been reinvestigated by Herman and co-workers [15] in a crossed-beam scattering experiment. In addition to the charge transfer reaction (1) listed above, chemical reaction (5) leading to CF_2D^+ formation reported earlier [14], was also examined



In their evaluation of reaction heats the authors used a value of $IE(CF_2^{++})$ derived from the appear-

ance potential (AP) measurements [10] and noted the discrepancy between this value and that reported by Price et al. [14], 21.1 eV (486.6 kcal/mol).

In the past two decades only a few theoretical calculations have appeared on the CF_n^{++} dications. Koch and Frenking [16] performed MP2/6-31G* calculations for a series of CF_n ions including CF^{++} and CF_2^{++} . They found that the potential energy surface of CF_2^{++} exhibits a minimum for the linear structure, which is, considering the spin conservation rule, very stable toward fragmentation



The spin forbidden dissociation leading to the ground state $F^+(^3P)$ was found to be exothermic by 12.0 kcal/mol. The MP2/6-31G* calculated adiabatic ionization energies were 8.6 eV for CF, 25.5 eV for CF^+ , 10.8 eV for CF_2 , and 20.5 eV for CF_2^+ .

Multireference configuration interaction (MRCI) calculations have been performed by Senekowitsch et al. for the ground ($^1\Sigma$ and $^2\Sigma$) and first excited states ($^3\Pi$ and $^2\Pi$) of CF^+ [17] and CF^{++} [18]. The singlet–triplet separation for CF^+ was found to be 4.77 eV at the MRCI/cc-pVTZ level. The $^2\Sigma \rightarrow ^2\Pi$ excitation energy was theoretically predicted as 2.81 eV. The calculated values of the adiabatic IE were 9.17 eV for CF and 26.29 eV for CF^+ . In addition, HF/6-31G* calculations [19] and MP2/6-31G* [20] of CF_4^+ and CF_3^+ were carried out by De La Vega and San Fabian. The CF_3^{++} dication was also investigated. However, only D_{3h} symmetric geometries were considered in these studies and no vibrational frequencies were given.

The discrepancy in the heat of formation of CF_2^{++} obtained from charge transfer measurements [8,14] and from AP [10] motivated us to consider a closer examination of this problem by theoretical methods. In this communication we report on a theoretical investigation of the CF_n^{++} systems using a highly correlated and uniform level of theory. We employed the coupled cluster single double (triple) [CCSD(T)] method with a reasonably large and flexible basis set. This method is expected to deliver relative energies with absolute errors in the order of only few kcal/mol

[21–23]. To crosscheck the results of our calculations, we compared the estimates for individual singly charged fragments with energetics derived from experimental results.

2. Computational details

For energy calculations the coupled cluster method CCSD(T) [24–27] was used in conjunction with Dunning's correlation consistent triple zeta basis set (cc-pVTZ) with two *d* and one *f* polarization functions [28–30] as implemented in the MOLPRO97 program. The geometry was preoptimized at the density functional level (DFT) using the same basis set. The parametrized hybrid method, due to Becke [31,32], which involves a semiempirical combination of an "exact" (i.e. Hartree-Fock-like, but based on Kohn-Sham orbitals) exchange, and the gradient-corrected Becke exchange [33] and Lee-Yang-Parr correlation [34] functionals. DFT calculations were performed with the GAUSSIAN94 [35] program. In analogy with the GAUSSIAN keywords, this approximate DFT method will be referred to as B3LYP. From our previous studies we expect that the geometries and energies calculated with the B3LYP method will be at least of MP2/DZP quality [36–38] and should serve as good initial estimates for CCSD(T) calculations.

The CCSD(T) calculations were performed with the MOLPRO97 [39] program package using the restricted (open shell) coupled cluster code [40] based on restricted Hartree-Fock (RHF) orbitals. The 1s electrons at the carbon and fluorine atoms were kept frozen in the energy calculation. The geometry was also optimized at this level, using numerical first and second derivatives of the energy starting from the structures obtained at B3LYP. The following point group symmetries were kept during the optimization (for the nonabelian point groups, the calculations were actually performed exploiting the corresponding highest abelian subgroup): C_{2v} ($D_{\infty h}$) for CF_2 (CF_2^{++}), C_{3v} (D_{3h}) for CF_3 (CF_3^+), and T_d for CF_4 . For the CF_3^{++} we used both the C_{2v} and D_{3h} symmetries and found a sizable Jahn-Teller distortion [41].

3. Results and discussion

The B3LYP and CCSD(T) geometries, total energies and harmonic vibrational frequencies of neutral, singly and doubly charged CF_n ($n = 1, 2$, and 3) are listed in Table 1. Their ionization energies, electron affinities and reaction enthalpies from our calculations are summarized in Table 2 together with the experimental reference data. The CCSD(T) calculated ionization energies compare well with the experiment. The largest deviation was found for the fluorine atom, where the CCSD(T) calculation yields 17.13 eV, compared with recent experimental values of 17.20 eV [42] and 17.423 eV [43]. Since the latter value is more reliable, we are left with an error of $\Delta E = 0.29$ eV. It can be shown [44] that the role of the one-electron basis is essential in the calculations of the IE(F) [CCSD(T)/aug-cc-pVQZ; IE(F) = 17.34 eV]. On the other hand, the CCSD(T)/cc-pVTZ calculated electron affinity of fluorine (3.32 eV) compares well with the experimental value of 3.40 eV.

Probably the best experimental IE value for $CF(^2\Pi)$, 9.11 ± 0.01 eV, was obtained from photoelectron spectroscopy measurements by Dyke et al. [45]. The value is very close ($\Delta E = 0.16$ eV) to our calculated adiabatic ionization energy of 8.95 eV. A further indication of the quality of our calculated results is the $^1\Sigma \rightarrow ^3\Pi$ separation for CF^+ ; our calculations give 4.79 eV, in excellent agreement with other theoretical MRCI value of 4.77 eV [18]. Our calculated value of IE(CF^+) is 25.84 eV, again in agreement with both the MRCI calculations (26.29 eV) and the experimental charge stripping value of 26.0 ± 0.4 eV [11]. Similarly, our calculated adiabatic IE(CF_2), 11.20 eV, is only 0.24 eV lower than the very recent photoionization value of 11.445 ± 0.025 eV [46]. The ionization energy of CF_3 , calculated by us, 8.77 eV, agrees well with the recent experimental result of 8.76 eV obtained from mass spectrometric equilibrium measurements [47]. Finally, CCSD(T) calculations gave 26.80 eV for the IE(CF_3^+); that is in agreement with the experimental value of 26.30 ± 0.3 eV [11]. In general, it appears that these directly calculated ionization energies of the CF_n^+ fragments are reliable within ± 0.2 eV.

Table 1

Calculated energies, geometries, and frequencies for CF₄ and its fragments

		E_{tot} (Hartree)	R_{CF} (Å)	α_{FCF}	Frequencies (cm ⁻¹)
F(² P)	B3LYP	−99.762 866			
	CCSD(T)	−99.620 361			
F ⁺ (³ P)	B3LYP	−99.113 922			
	CCSD(T)	−98.990 795			
F ⁺ (¹ S)	B3LYP	−98.980 429			
	CCSD(T)	−98.898 512			
F [−] (¹ S)	B3LYP	−99.850 170			
	CCSD(T)	−99.742 359			
CF(² Π)	B3LYP	−137.835 253	1.276		σ 1304.8
	CCSD(T)	−137.604 560	1.278		σ 1321.3
CF(⁴ Σ)	B3LYP	−137.699 438	1.328		σ 1228.3
	CCSD(T)	−137.475 738	1.330		σ 1245.5
CF ⁺ (³ Π)	B3LYP	−137.321 870	1.214		σ 1613.7
	CCSD(T)	−137.099 269	1.127		σ 1614.4
CF ⁺ (¹ Σ)	B3LYP	−137.488 873	1.157		σ 1792.0
	CCSD(T)	−137.275 569	1.161		σ 1787.3
CF ⁺⁺ (² Σ)	B3LYP	−136.536 513	1.126		σ 1990.2
	CCSD(T)	−136.325 952	1.132		σ 1949.7
CF ₂ (¹ A ₁)	B3LYP	−237.792 855	1.305	104.6	a ₁ 670.2 b ₂ 1113.5 a ₁ 1231.5
	CCSD(T)	−237.419 132	1.302	104.9	a ₁ 672.9 b ₂ 1162.7 a ₁ 1256.8
CF ₂ (³ B ₁)	B3LYP	−237.708 680	1.318	119.7	a ₁ 510.8 a ₁ 1136.9 b ₂ 1303.5
	CCSD(T)	−237.329 188	1.317	119.4	a ₁ 516.9 a ₁ 1162.6 b ₂ 1346.4
CF ₂ ⁺ (² A ₁)	B3LYP	−237.379 819	1.220	124.6	a ₁ 643.2 a ₁ 1364.7 b ₂ 1678.4
	CCSD(T)	−237.007 645	1.220	124.8	a ₁ 647.3 a ₁ 1373.9 b ₂ 1708.4
CF ₂ ⁺⁺ (¹ Σ _g)	B3LYP	−236.612 817	1.150	180.0	π _u 559.6 σ _g 1211.9 σ _u 2341.9
	CCSD(T)	−236.251 070	1.153	180.0	π _u 557.7 σ _g 1199.3 σ _u 2330.5
CF ₃ (² A ₁)	B3LYP	−337.696 293	1.321	111.3	e 504.7 a ₁ 697.5 a ₁ 1082.2 e 1243.5
	CCSD(T)	−337.172 609	1.317	111.4	Not calculated
CF ₃ ⁺ (¹ A ₁)	B3LYP	−337.363 972	1.236	120.0	e' 588.3 a ₂ ' 798.9 a ₁ ' 1051.3 e' 1665.6
	CCSD(T)	−336.850 236	1.233	120.0	e' 588.3 a ₂ ' 798.9 a ₁ ' 1051.3 e' 1665.7
CF ₃ ⁺⁺ (² A ₁)	B3LYP	−336.447 183	1.564	109.9	b ₂ 321.4 a ₁ 371.3 a ₁ 606.4
			1.186		b ₁ 653.6 a ₁ 1260.0 b ₂ 1951.4
	CCSD(T)	−335.899 050	1.655	110.0	b ₂ 355.9 a ₁ 455.0 a ₁ 656.9
			1.186		b ₁ 669.6 a ₁ 1285.5 b ₂ 1995.2
CF ₄ (¹ A _{1g})	B3LYP	−437.661 627	1.326	109.5	e 429.2 t 622.6 a ₁ 903.9 t 1256.9
	CCSD(T)	−437.001 103	1.319	109.5	Not calculated

To assess further the quality of the CCSD(T) calculations, we computed reaction enthalpies (ΔH_R) for several arbitrarily chosen reactions (some listed in Table 2) and compared them with the thermochemical values, determined from experimental heats of formation [8]. The results were encouraging: for the entire series, deviations between theory and experiment never exceeded 5 kcal/mol. Finally, it should be noted that deviancies between theory and experiment for the B3LYP method follow the same trend as the strict ab initio calculations. The absolute errors are, however,

larger, being around ± 0.5 eV (11 kcal/mol). One notable exception is the disappointing failure of the B3LYP functional to describe the ionization energy of CF₃⁺. The B3LYP results deviate here by more than 1.5 eV from the CCSD(T) as well as from the experimental value. It is known that, contrary to the methods based on wave function, the effect of the incomplete basis is much smaller for DFT approaches [48–50] and thus we cannot expect any further improvement when using larger basis sets.

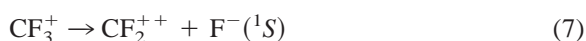
We have chosen three different reactions to esti-

Table 2
Calculated IE and ΔH_R of several dissociation reactions

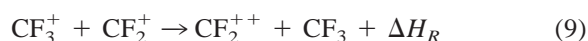
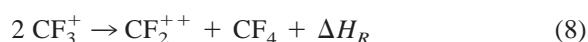
	B3LYP cc-pVTZ (eV)	CCSD(T) cc-pVTZ(spdf) (eV)	Expt. IE (eV)	Error CCSD(T) (eV)
F(EA)	2.38	3.32	3.40	0.08
F(IE)	17.66	17.13	17.42	0.29
CF(IE)	9.43	8.95	9.11	0.16
CF ⁺ (IE)	25.92	25.84	26.0	0.16
CF ₂ (IE)	11.24	11.20	11.44	0.24
CF ₂ ⁺ (IE)	20.87	20.59		
CF ₃ (IE)	9.04	8.77	8.76	−0.01
CF ₃ ⁺ (IE)	25.12	26.80	26.6	−0.20

Reactions	B3LYP (kcal/mol)	CCSD(T) (kcal/mol)	ΔH_R expt. (kcal/mol)	Error CCSD(T) (kcal/mol)
CF ₄ → CF ₃ + F	127.05	130.61	129.64	−0.97
CF ₄ → CF ₃ ⁺ + F + e [−]	335.59	332.90	337.00	4.10
CF ₄ → CF ₃ ⁺ + F [−]	280.80	256.34	253.14	−3.20
CF ₃ → CF ₂ + F	88.21	83.53	87.90	4.37
CF ₃ → CF ₂ ⁺ + F [−]	292.61	265.19	267.60	2.41
CF ₃ ⁺ → CF ₂ ⁺ + F	138.86	139.45	144.10	4.65

mate of the heat of formation of CF₂⁺⁺ dication (Table 3). (1) A direct calculation based on the heat of formation of CF₂⁺ (214.6 kcal/mol [8]) and theoretically calculated value of its IE; this leads to $\Delta H_f(\text{CF}_2^{++}) = 689.4$ kcal/mol. (2) The dissociation reaction



using $\Delta H_f(\text{CF}_3^+) = 89.5$ kcal/mol and $\Delta H_f(\text{F}^-) = 59.4$ kcal/mol [8], together with the CCSD(T) calculated bond energy; this gives $\Delta H_f(\text{CF}_2^{++}) = 686.6$ kcal/mol. (3) Calculations based on two isodesmic reactions



using $\Delta H_f(\text{CF}_3) = -112.4$ kcal/mol and $\Delta H_f(\text{CF}_4) = 223.0$ kcal/mol [8], and the reaction enthalpies calculated with the use of the CCSD(T) method (281.3 and 272.5 kcal/mol); this yields values for $\Delta H_f(\text{CF}_2^{++})$ of 683.4 kcal/mol [reaction (8)] and 689.0 kcal/mol [reaction (9)].

Thus, there is a satisfying consistence in the results for all model reactions. In summary we conclude that, based on our calibration study described previously, the heat of formation of the difluorocarbene dication (CF₂⁺⁺) is of 687 ± 5 kcal/mol (29.8 ± 0.2 eV). This is in good agreement with the value derived earlier by Leone et al [12,13] from studies of charge transfer between CF₂⁺⁺ and rare gas ions. However, it is considerably smaller than the value derived from electron impact appearance potential measurement of CF₂⁺⁺ from CF₄ (42.9 ± 0.3 eV [10]), $\Delta H_f(\text{CF}_2^{++}) = 732 \pm 7$ kcal/mol (31.7 ± 0.3 eV), and which was used earlier [15]. The latter value is so high that the difference (~ 2 eV) cannot be accounted

Table 3
Estimation of $\Delta H_f(\text{CF}_2^{++})$ and the reactions used

Reaction	Estimated $\Delta H_f(\text{CF}_2^{++})$	
	B3LYP (kcal/mol)	CCSD(T) (kcal/mol)
CF ₂ ⁺ → CF ₂ ⁺⁺ + IE(CF ₂ ⁺)	695.89	689.35
CF ₃ ⁺ → CF ₂ ⁺⁺ + F [−] + BDE	714.28	686.56
2CF ₃ ⁺ → CF ₂ ⁺⁺ + CF ₄ + ΔH_R	686.62	683.35
CF ₃ ⁺ + CF ₂ ⁺ → CF ₂ ⁺⁺ + CF ₃ + ΔH_R	689.27	688.97

for by unfavorable Franck-Condon factors and suggests that electron impact ionization of CF_4 does not initially produce ground state CF_2^{++} .

Acknowledgements

The computational work was made possible by generous support of the Volkswagenstiftung [research grant for three of the authors (W.K., J.H., and Z.H.)]. The project was also partially supported by grant nos. 203/97/0351 and 440410 of the Grant Agency of the Czech Republic and the Grant Agency of the Academy of Sciences, respectively, and by the Deutsche Forschungsgemeinschaft. The authors are grateful to Professor S. Iwata (IMS) for many helpful discussions.

References

- [1] M. Larson, Comments At. Mol. Phys. 29 (1993) 39.
- [2] D. Mathur, Phys. Rep. 225 (1993) 193.
- [3] W. Koch, F. Maquin, D. Stahl, H. Schwarz, Chimia 39 (1985) 376.
- [4] K. Lammertsma, P.v.R. Schleyer, H. Schwarz, Angew. Chem. Int. Ed. Engl. 28 (1989) 1321.
- [5] J.A. Mucha, D.W. Hess, Am. Chem. Soc. Symp. 219 (1983) 215.
- [6] J.W. Coburn, Plasma Chem. Plasma Proc. 2 (1982) 1.
- [7] J.C. Martz, D.W. Hess, W.E. Anderson, Plasma Chem. Plasma Proc. 10 (1990) 261.
- [8] In this article we use the latest thermochemical data from the NIST Standard Reference Database Number 69–February 1997 Release, which is available in the Internet at the location <http://webbook.nist.gov/chemistry>. The neutral thermochemical data were compiled by H.Y. Afeefy, J.F. Liebman, S.E. Stein. The ionization energetics (IE, AE) is compiled by S.G. Lias, H.M. Rosenstock, K. Draxl, B.W. Steiner, J.T. Herron, J.L. Holmes, R.D. Levin, J.F. Liebman, S.A. Kafafi. The proton affinity data are compiled and evaluated by E.P. Hunter, S.G. Lias. The mass and IR spectra were compiled by NIST Mass Spectrometry Data Center, S.E. Stein. The Web-Book program was written by P.J. Linstrom. The general editor is W.G. Mallard.
- [9] M.M. Bibby, B.J. Toubelis, G. Carter, Electron. Lett. 1 (1965) 50.
- [10] K. Stephan, H. Deutsch, T.D. Mark, J. Chem. Phys. 83 (1985) 5712.
- [11] C.J. Proctor, C.J. Porter, T. Ast, J.H. Beynon, Int. J. Mass Spectrom. Ion Phys. 41 (1982) 251.
- [12] S.D. Price, M. Manning, S.R. Leone, Chem. Phys. Lett. 214 (1993) 553.
- [13] M. Manning, S.D. Price, S.R. Leone, J. Chem. Phys. 99 (1993) 8695.
- [14] S.D. Price, M. Manning, S.R. Leone, J. Am. Chem. Soc. 116 (1994) 8673.
- [15] Z. Dolejšek, M. Fárník, Z. Herman, Chem. Phys. Lett. 235 (1995) 99.
- [16] W. Koch, G. Frenking, Chem. Phys. Lett. 114 (1985) 178.
- [17] K.A. Peterson, R.C. Woods, P. Rosmus, H.J. Werner, J. Chem. Phys. 93 (1990) 1889.
- [18] J. Senekowitsch, S.V. O'Neil, H.J. Werner, P.J. Knowles, J. Chem. Phys. 93 (1990) 562.
- [19] J.M. De La Vega, E. San Fabian, Int. J. Quantum. Chem. 52 (1994) 947.
- [20] J.M. De La Vega, E. San Fabian, Chem. Phys. 151 (1991) 335.
- [21] See, e.g., P.R. Taylor, in Lecture Notes in Quantum Chemistry II, B.O. Roos (Ed.), Springer, Berlin, 1994.
- [22] T.J. Lee, G.E. Scuseria, in Quantum Chemical Electronic Structure Calculations with Chemical Accuracy, S.R. Langhoff (Ed.), Kluwer Academic, Dordrecht, 1995.
- [23] R.J. Bartlett, J.F. Stanton, in Reviews in Computational Chemistry, K.B. Lipkowitz, D.B. Boyd (Ed.), VCH, New York, 1994, vol. 5.
- [24] J. Čížek, Adv. Chem. Phys. 14 (1969) 35.
- [25] G.D. Purvis, R.J. Bartlett, J. Chem. Phys. 76 (1982) 1910.
- [26] G.E. Scuseria, C.L. Janssen, H.F. Schaefer III, J. Chem. Phys. 89 (1988) 7382.
- [27] G.E. Scuseria, H.F. Schaefer III, J. Chem. Phys. 90 (1989) 3700.
- [28] T.H. Dunning Jr., J. Chem. Phys. 90 (1989) 1007.
- [29] R.A. Kendall, T.H. Dunning Jr., R.J. Harrison, J. Chem. Phys. 96 (1992) 6796.
- [30] D.E. Woon, T.H. Dunning Jr., J. Chem. Phys. 98 (1993) 1358.
- [31] A.D. Becke, J. Chem. Phys. 98 (1993) 1372.
- [32] A.D. Becke, J. Chem. Phys. 98 (1993) 5648.
- [33] A.D. Becke, J. Chem. Phys. 84 (1986) 4524.
- [34] C. Lee, W. Yang, R.G. Parr, Phys. Rev. B 37 (1988) 785.
- [35] GAUSSIAN 94, M.J. Frisch, G.W. Trucks, H.B. Schlegel, P.M.W. Gill, B.G. Johnson, M.A. Robb, J.R. Cheeseman, T. 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, J.A. Pople, Gaussian, Inc., Pittsburgh, PA, 1995.
- [36] J. Hrušák, D. Schröder, R.H. Hertwig, P. Schwerdfeger, W. Koch, H. Schwarz, Organometallics 14 (1995) 1284.
- [37] R.H. Hertwig, J. Hrušák, D. Schröder, W. Koch, H. Schwarz, Chem. Phys. Lett. 236 (1995) 194.
- [38] J. Hrušák, D. Schröder, H. Schwarz, S. Iwata, Bull. Chem. Soc. Jpn. 70 (1997) 777.
- [39] MOLPRO is a package of ab initio programs written by H.-J. Werner, P.J. Knowles, with contributions from J. Almlöf, R.D. Amos, A. Berning, D.L. Cooper, M.J.O. Deegan, A.J. Dobbyn, F. Eckert, S.T. Elbert, C. Hampel, R. Lindh, A.W. Lloyd, W. Meyer, A. Nicklass, K. Peterson, R. Pitzer, A.J. Stone, P.R. Taylor, M.E. Mura, P. Pulay, M. Schütz, H. Stoll, T. Thorsteinsson.

- [40] P.J. Knowles, C. Hampel, H.-J. Werner, J. Chem. Phys. 99 (1993) 5219.
- [41] J. Hrušák, N. Sändig, W. Koch, Int. J. Mass Spectrom. Ion Processes 185/186/187 (1999) 701.
- [42] M.V. Veljkovic, O.M. Neskovic, K.F. Zmbov, J. Serb. Cem. Soc. 57 (1992) 753.
- [43] CRC Handbook of Chemistry and Physics: A Ready-Reference book of Chemical and Physical data, Editors D.R. Lide, H.P.R. Frederikse, 77. edition, Boca Raton, CRC Press, 1996.
- [44] J. Hrušák, Z. Herman, S. Iwata, Int. J. Mass Spectrom. 192 (1999) 165.
- [45] J.M. Dyke, A.E. Lewis, A. Moris, J. Chem. Phys. 80 (1982) 1382.
- [46] T.J. Buckley, R.D. Johnson, R.E. Huie, Y. Yhang, S.C. Kuo, R.B. Klemm, J. Chem. Phys. 99 (1995) 4879.
- [47] M. Tsuji, M. Aizawa, Y. Nishimura, Chem. Lett. 3 (1995) 211.
- [48] J. Hrušák, H. Friedrichs, H. Schwarz, H. Razafinjanahary, H. Chermette, J. Phys. Chem. 100 (1996) 100.
- [49] J. Hrušák, S. Iwata, J. Chem. Phys. 106 (1997) 4877.
- [50] J. Hrušák, J. Žabka, Z. Dolejšek, Z. Herman, Int. J. Mass Spectrom. Ion Phys. 167/168 (1997) 675.