

Accurate *ab initio* calculations of the ground states of FeC, FeC⁺, and FeC⁻

Demeter Tzeli¹ and Aristides Mavridis^{2,a)}¹*Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation, 48 Vassileos Constantinou Ave., Athens 116 35, Greece*²*Department of Chemistry, Laboratory of Physical Chemistry, National and Kapodistrian University of Athens, P.O. Box 64 004, Zografou, Athens 157 10, Greece*

(Received 15 March 2010; accepted 23 April 2010; published online 20 May 2010)

For the ground states of the diatomic carbide FeC($X^3\Delta$) and its ions, FeC⁺($X^2\Delta$) and FeC⁻($X^2\Delta$), we report on accurate multireference variational *ab initio* results employing augmented correlation consistent basis sets of quintuple cardinality. The dissociation energies and bond lengths are found to be $D_0^0=87 \pm 1$, 95.2, and 84 ± 1 kcal/mol at $r_e=1.581$, 1.556, and 1.660 Å for FeC, FeC⁺, and FeC⁻, respectively. All our final numbers are in agreement with the available experimental data.

© 2010 American Institute of Physics. [doi:10.1063/1.3429612]

I. INTRODUCTION

In a sequence of four papers, we examined the electronic structure and bonding of FeC (Refs. 1 and 2) and FeC⁺ (Ref. 3) by high level multireference and coupled cluster calculations. In particular, we have published full potential energy curves (PECs) for 41 FeC and 40 FeC⁺ states, reporting on energetics and spectroscopic parameters. Table I compares theoretical and experimental results of the ground states of FeC($X^3\Delta$) and FeC⁺($X^2\Delta$). Given the abstruseness of these chemically “simple” but otherwise fastidious species, it can be seen that the agreement between theory and experiment is satisfactory. It is interesting to observe that there is no accurate experimental dissociation energy of either FeC or FeC⁺, whereas experimental results on FeC⁻ are completely missing. As a matter of fact, the listed experimental dissociation energy D_0 of FeC has been obtained indirectly through the energy conservation relation,

$$D_0(\text{FeC}) = \text{IE}(\text{FeC}) + D_0(\text{FeC}^+) - \text{IE}(\text{Fe}). \quad (1)$$

Using the experimental ionization energy (IE) of FeC by Brugh and Morse,¹² the experimental D_0 of FeC⁺,¹⁰ and the IE of Fe (Ref. 13), the following is obtained:

$$\begin{aligned} D_0(\text{FeC}) &= 7.74 \pm 0.09 \text{ (Ref. 12)} \\ &+ 4.1 \pm 0.3 \text{ (Ref. 10)} - 7.9024 \text{ (Ref. 13)} \\ &= 3.9 \pm 0.4 \text{ eV} = 90 \pm 9 \text{ kcal/mol} \end{aligned}$$

or

$$D_e = D_0 + \omega_e/2 \text{ (Ref. 6)} = 91 \pm 9 \text{ kcal/mol.}$$

A very accurate experimentally determined IE of FeC, published recently by Chang *et al.*,⁹ $\text{IE}(\text{FeC}) = 7.59318 \pm 0.00006$ eV, allows for a better $D_0(D_e)$ estimate of FeC and an accurate determination of the difference $D_0(\text{FeC}^+) - D_0(\text{FeC})$ using relation (1): $D_0(\text{FeC}) = 87.4 \pm 9$ kcal/mol or $D_e = 88.6 \pm 9$ kcal/mol and $D_0(\text{FeC}^+) - D_0(\text{FeC}) = 7.9024$ (Ref. 13) - 7.59318 (Ref. 9)

= 0.3092 eV. The latter is in complete agreement with the MRCI+Q/[7s6p4d3f2g/Fe cc-pVQZ/C] results of Tzeli and Mavridis^{1,3} (see Table I). Indeed, $D_0(\text{FeC}^+) - D_0(\text{FeC}) = 97.6$ (Ref. 3) - 90.5 (Ref. 1) kcal/mol = 0.308 eV.

Motivated by the experimental work of Chang *et al.*,⁹ as well as the high level theoretical coupled-cluster, but somehow controversial CCSDTQ work of Lau *et al.*⁴ on FeC and FeC⁺ (*vide infra*), we decided to carry out state-of-the-art multireference (complete active space self-consistent field + single + double replacements = CASSCF + 1 + 2 = MRCI) calculations, combined with large basis sets for the ground states of FeC, FeC⁺, and FeC⁻. The purpose of the present work is the definitive determination of dissociation energies and spectroscopic parameters of FeC, FeC⁺, and FeC⁻. No experimental or *ab initio* results exist in literature on FeC⁻, apart from two density functional theory calculations, BPW91/6-311+G(d) [Ref. 14(a)] and B3LYP/6-311+G(d) [Ref. 14(b)], published in 2003 and 2009, respectively¹⁴. Both groups predicted correctly that the ground state of FeC⁻ is $X^2\Delta$.

II. METHODS

For the Fe and C atoms, the augmented weighted core aug-cc-pwCV5Z=(31s23p15d6f5g4h3i) (Ref. 15) and the aug-cc-pV5Z=(15s9p5d4f3g2h) (Ref. 16) basis sets were generally contracted to [12s11p9d6f5g4h3i/Fe 7s6p5d4f3g2h/C], a total of 387 spherical Gaussians. For the scalar relativistic calculations, similar but suitably contracted basis sets aug-cc-pwCV5Z-DK (Ref. 15) and cc-pV5Z-DK (Ref. 16) for the Fe and C atoms were used, respectively. To the plain cc-pV5Z-DK relativistic basis for the C atom, a complete set of diffuse functions 1s+1p+1d+1f+1g+1h were attached taken from the aug-cc-pV5Z set.

The reference CASSCF wave functions were created by distributing 12e⁻ (FeC), 11e⁻ (FeC⁺), and 13e⁻ (FeC⁻) to ten “valence” orbitals (4s+3d/Fe+2s+2p/C). Subsequent internally contracted (ic) MRCI calculations (=CASSCF+1+2) included the subvalence 3s²3p⁶ electrons of the metal

^{a)}Electronic mail: mavridis@chem.uoa.gr.

TABLE I. Comparison of the previous theoretical and experimental results of the ground states of FeC($X^3\Delta$) and FeC⁺($X^2\Delta$).

Method ^a	r_e (Å)	D_e (kcal/mol)	ω_e (cm ⁻¹)	μ (D)
FeC				
C-MRCI+Q ^b	1.582	90.5 ^c	877	
C-MRCI+Q ^d	1.579	93.8 ^c	880	2.07
UCCSD(T) ^e	1.561	87.1 ^f	1373	
Expt.	1.596 ^g	91 ± 9 ^h	862.9 ± 6.2 ⁱ	2.36 ± 0.03 ^j
	1.591 ^k		866.6 ± 8.2 ^l	
	1.588 941 4 ^m		866.919 ^m	
FeC⁺				
C-MRCI+Q ⁿ	1.557	103.3 ^o (97.6 ^p)	944.2	
C-MRCI+DKH2+Q ⁿ	1.555	107 ^o (101 ^p)	928	
UCCSD(T) ^e	1.546	94.8 ^f	1440	
Expt.	1.559 ^q	94 ± 7 ^r	927.14 ^s	
		84.2 ± 4.1 ^s		

^a+Q and DKH2 refer to the Davidson correction for unlinked clusters and to second order Douglas–Kroll–Hess scalar relativistic corrections. MRCI=CASSCF+1+2; C-MRCI means that the Fe 3s²3p⁶ subvalence electrons have been included in the CI.

^bReference 1; basis set: [7s6p4d3f2g/Fe cc-pVQZ/C].

^cWith respect to the adiabatic atoms Fe(³D)+C(³P).

^dReference 2; basis set: [7s6p4d3f2g1h/Fe aug-cc-pVQZ/C].

^eReference 4; basis set: aug-cc-pwCV5Z.

^fReference 4; D_0 value obtained through the UCCSD(T) CBS limit+corrections (see text).

^gReference 5; r_0 value of $X^3\Delta_3$ state; electronic and rotational spectroscopy.

^hIndirectly obtained through the experimental D_0 value of FeC⁺ (see text and Ref. 1).

ⁱReference 6; dispersed fluorescence spectroscopy.

^jReference 7; optical Stark spectroscopy.

^kReference 5; r_0 value of $X^3\Delta_2$ state; electronic spectroscopy.

^lReference 6; $X^3\Delta_2$ state; dispersed fluorescence spectroscopy.

^mReference 8; near-infrared diode laser spectroscopy.

ⁿReference 3; basis set: [7s6p4d3f2g/Fe cc-pVQZ/C].

^o D_e with respect to the adiabatic fragments Fe⁺(⁴F)+C(³P).

^p D_e with respect to the ground state fragments Fe⁺(⁶D)+C(³P).

^qReference 9; two color laser photoionization and photoelectron spectroscopy.

^rReference 10; D_0 value; gas-phase photodissociation of FeCH₂⁺.

^sReference 11; threshold photoionization study of Fe(CO)₃.

(C-MRCI). The ic-MRCI(C-MRCI) expansions for FeC, FeC⁺, and FeC⁻ contain 77×10^6 (16×10^9), 99×10^6 (17×10^9), and 42×10^6 (10×10^9) configurations. Scalar relativistic effects were taken into account through the Douglas–Kroll–Hess (DKH n)^{17,18} approach of $n=2-8$. Size nonextensivity errors, quite large as expected for C-MRCIs of $19e^-$ (FeC)– $21e^-$ (FeC⁻), were mitigated through the Davidson (+Q) (Ref. 19) and the averaged coupled pair functional (ACPF) (Ref. 20) approximations.

An effort to perform coupled-cluster calculations at the RCCSD(T)/[aug-cc-pwCV5Z/Fe aug-cc-pV5Z/C] level failed for both FeC and FeC⁻ species due to severe convergence problems. Although RCCSD(T) calculations were feasible for the FeC⁺ cation, the results were not deemed reliable enough as to be reported. All calculations were performed by the MOLPRO, version 2006.1, program.²¹

III. RESULTS AND DISCUSSION

A. FeC($X^3\Delta$)

Table II lists all numerical results of this work; as is evinced, scalar relativistic effects have been practically converged at the second order, $n=2$. With the exception of the

total energy which, for instance, at the C-ACPF level converges at the fourth DKH order, all the other properties remain in essence the same for DKH orders from $n=2$ to $n=8$. At the highest level of theory, C-MRCI+DKH8+Q(C-ACPF+DKH8), $D_e^0=89.2$ (86.7), or $D_0^0(=D_e^0-\omega_e/2)=87.9$ (85.4) kcal/mol with respect to Fe(⁵D)+C(³P) at $r_e=1.576$ (1.581) Å. The bond distance is in good agreement with the experimental value, being shorter from the latter by ~ 0.01 Å. As to the dissociation energy, our recommended value is $D_e^0(D_0^0)=88 \pm 1$ (87 ± 1) kcal/mol, in agreement with the predicted value $D_0^0=87.1$ kcal/mol at $r_e=1.561$ Å by Lau *et al.*⁴ Their D_0^0 value is the complete basis set (CBS) limit of UCCSD(T)/aug-cc-pwCV5Z+ ΔE_{ZPVE} (experimental vibrational frequencies)+corrections for spin-orbit+scalar relativistic effects+higher order excitation effects (up to “T+Q”/aug-cc-pVQZ for T and cc-pVTZ for Q) at the r_e distance of the UCCSD(T)/aug-cc-pwCV5Z level of theory.⁴ Moreover, at our highest level, $\mu_{FF}=2.15$ D obtained by the finite field method, in acceptable agreement with the experimental value of Steimle and co-workers,⁷ $\mu=2.36 \pm 0.03$ D. Notice, however, that the dipole moment calculated as an expectation value, $\langle \mu \rangle=1.40$ D, is in com-

TABLE II. Absolute energies $E(E_h)$, bond lengths r_e (Å), binding energies D_e (kcal/mol), harmonic frequencies and anharmonic corrections ω_e , $\omega_e x_e$ (cm⁻¹), rotational vibrational coupling constants α_c (cm⁻¹), centrifugal distortions \bar{D}_e (cm⁻¹), Mulliken charges on Fe q_{Fe} , and dipole moments $\langle \mu \rangle$ (D) of the ground states of ⁵⁶Fe¹²C, ⁵⁶Fe¹²C⁺, and ⁵⁶Fe¹²C⁻ at the C-MRCI, C-MRCI+Q, and C-ACPF/aug-cc-pwCV5Z(-DK)_{Fe}/aug-cc-pV5Z(-DK)_C levels of theory.

Methods ^a	-E	r_e	D_e	ω_e	$\omega_e x_e$	$\alpha_c(10^{-3})$	$\bar{D}_e(10^{-6})$	q_{Fe}	$\langle \mu \rangle$	μ_{FF}^b
FeC($X^3\Delta$)										
C-MRCI	1300.970 860	1.5774	86.36	893.0	8.61	6.62	1.62	0.45	1.17	1.82
C-MRCI+Q	1301.040 42	1.5780	91.28	907.8	6.68	5.82	1.56			2.01
C-MRCI+DKH2	1309.866 317	1.5755	84.20	897.6	6.84	6.91	1.61	0.44	1.35	1.98
C-MRCI+DKH2+Q	1309.936 10	1.5759	89.06	912.9	4.78	6.07	1.56			2.15
C-MRCI+DKH8	1309.903 523	1.5755	84.79	898.2	10.7	5.94	1.61	0.44	1.35	1.98
C-MRCI+DKH8+Q	1309.973 31	1.5759	89.18	913.5	8.98	5.47	1.56			2.16
C-ACPF	1301.047 369	1.5829	88.96	902.7	10.0	5.55	1.55	0.40	1.25	2.02
C-ACPF+DKH2	1309.943 191	1.5807	86.79	908.4	9.93	5.53	1.56	0.39	1.40	2.14
C-ACPF+DKH3	1309.982 053	1.5807	86.71	907.9	10.2	5.61	1.55	0.39	1.40	2.16
C-ACPF+DKH4	1309.980 183	1.5807	87.03	907.8	9.81	5.45	1.55	0.39	1.40	2.15
C-ACPF+DKH5	1309.980 429	1.5806	86.74	907.5	9.20	5.41	1.56	0.39	1.40	2.14
C-ACPF+DKH6	1309.980 393	1.5806	86.79	907.5	10.5	5.57	1.55	0.39	1.40	2.14
C-ACPF+DKH7	1309.980 397	1.5807	87.40	907.5	10.2	5.64	1.55	0.39	1.40	2.13
C-ACPF+DKH8	1309.980 396	1.5807	86.70	907.3	10.5	5.76	1.55	0.39	1.40	2.14
FeC⁺($X^2\Delta$)										
C-MRCI	1300.721 476	1.5506	94.01/99.90	944.6	5.45	5.97	1.60	1.19		
C-MRCI+Q	1300.780 38	1.5541	99.78/102.5	941.1	4.86	5.78	1.59			
C-ACPF	1300.782 132	1.5588	99.83/102.4	929.0	4.51	5.80	1.61	1.17		
C-MRCI+DKH8	1309.648 792	1.5479	90.64/104.3	956.8	10.1	5.58	1.58	1.18		
C-MRCI+DKH8+Q	1309.707 70	1.5509	96.41/106.8	953.2	9.97	5.52	1.57			
C-ACPF+DKH8	1309.709 522	1.5557	96.53/106.8	941.8	5.49	5.76	1.58	1.16		
FeC⁻($X^2\Delta$)										
MRCI ^c	1300.587 387	1.6132	84.28	869.5	12.2	6.37	1.49			
MRCI+Q ^c	1300.627 45	1.6130	91.38	872.0	9.14	5.11	1.48			
ACPF ^c	1300.633 019	1.614	92.28	896.7	8.98	4.90	1.40			
C-MRCI	1300.987 066	1.6079	86.62	875.5	15.0	7.40	1.50	-0.20		
C-MRCI+Q	1301.068 42	1.6046	89.17	898.3	10.8	5.72	1.44			
C-ACPF	1301.087 249	1.6086	90.63	892.9	10.7	5.69	1.44	-0.34		
C-MRCI+DKH8	1309.921 685	1.6036	78.32	904.4	3.36	3.82	1.43	-0.22		
C-MRCI+DKH8+Q	1310.003 53	1.5998	84.39	926.7	5.38	3.23	1.42			
C-ACPF+DKH8	1310.022 525	1.6042	86.68	917.5	5.49	3.17	1.39	-0.36		

^aAll calculations are internally contracted. C-MRCI or C-ACPF means that the $3s^2p^6$ subvalence electrons of Fe have been included in the configuration interaction. DKH n , $n=2-8$, where n is the order of DKH correction; +Q refers to the multireference Davidson correction.

^b $\langle \mu \rangle$ calculated as an expectation value, μ_{FF} by the finite field approach; field strength of 10^{-4} a.u.

^cBasis set: aug-cc-pV5Z_{Fe,C}.

plete disharmony with experiment (see also Ref. 2 for a discussion on $\langle \mu \rangle$ versus μ_{FF}). A total Mulliken charge transfer of about $0.4e^-$ from Fe to C is observed.

B. FeC⁺($X^2\Delta$)

With respect to the ground state fragments, Fe⁺(⁶D) + C(³P), the C-MRCI+DKH8+Q(C-ACPF+DKH8) dissociation energy is $D_e^0=96.4(96.5)$ kcal/mol or $D_0^0=95.0(95.2)$ kcal/mol at $r_e=1.551(1.556)$ Å, in accordance with the corresponding experimental values of $D_0^0=94 \pm 7$ kcal/mol (Ref. 10) and $r_e=1.559$ Å.⁹ Our D_0^0 and r_e values are in agreement as well as with the results of Ref. 4, $D_0^0=94.8$ kcal/mol and $r_e=1.546$ Å, at the UCCSD(T)/CBS limit+corrections (*vide supra*). With respect to the *adiabatic* end fragments, Fe⁺(⁴F)+C(³P), $D_e(D_0)=106.8(105.4)$ kcal/mol at both C-MRCI+DKH8+Q and C-ACPF+DKH8 approaches. The

experimental energy difference, however, $\Delta E(^4F \leftarrow ^6D)=0.248$ eV(=5.72 kcal/mol) is overestimated by at least 5 kcal/mol when scalar relativity is taken into account; thus, a more realistic dissociation energy with respect to Fe(⁴F) is $D_0=101 \pm 1$ kcal/mol.

The C-MRCI+DKH8+Q(C-ACPF+DKH8) IE is $IE=E(FeC; X^3\Delta)-E(FeC^+; X^2\Delta)+\Delta\omega_e/2=7.228(7.373)$ eV, in contrast to the very accurate experimental IE of Lau *et al.*,⁹ $IE=7.593 18 \pm 0.000 06$ eV, 0.220 eV larger than the ACPF value. On the other hand, the C-MRCI+DKH8+Q calculated difference $D_0^0(FeC^+)-D_0^0(FeC)=IE(Fe)-IE(FeC)=95.05(95.18)-87.87(85.40)$ kcal/mol = 0.311(0.424) eV is in complete conformity with the experimental value of 0.309 ± 0.001 eV,⁹ but by 0.115 eV larger at the corresponding C-ACPF+DKH8 level of theory. Obviously, with this kind of systems, the agreement obtained presently between experiment and theory can be considered as very satisfactory.

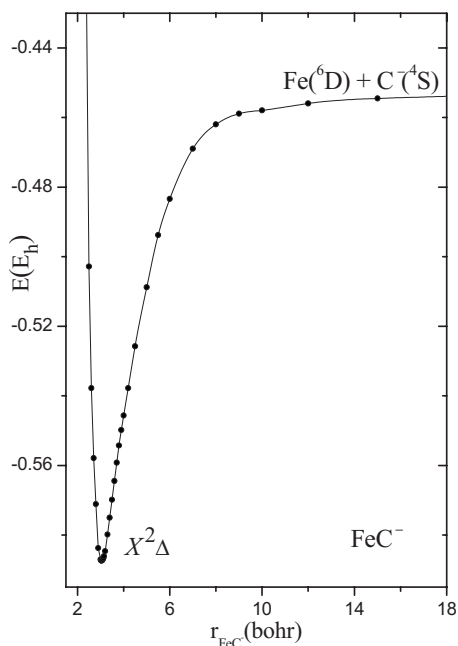


FIG. 1. MRCI/aug-cc-pV5Z_{FeC} PEC of the ground $X^2\Delta$ state of the FeC^- anion. Energies shifted by +1300.0 E_h .

C. $\text{FeC}^-(X^2\Delta)$

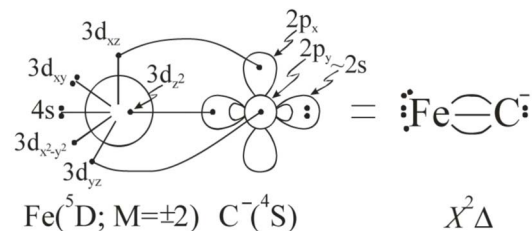
Our calculations show clearly that the ground state is of $^2\Delta$ symmetry, correlating to $\text{Fe}(^5D; 4s^2 3d^6) + \text{C}^-(^4S)$, with the first excited state, $a^4\Pi$, located about 16 kcal/mol higher; the MRCI PEC of $X^2\Delta$ is displayed in Fig. 1.

The dominant C-MRCI equilibrium configurations, corresponding Mulliken populations, and the valence-bond-Lewis diagram are the following (only valence electrons are counted for simplicity):

$$|X^2\Delta\rangle_{A_1} \approx |1\sigma^2 2\sigma^2 3\sigma^2 [0.78(1\pi_x^2 1\pi_y^2) - 0.17(1\pi_x^2 2\pi_y^2 + 2\pi_x^2 1\pi_y^2)] 1\delta_+^1 1\delta_-^2\rangle,$$

$$4s^{1.21} 4p_z^{0.42} 3d_{z^2}^{1.27} 3d_{xz}^{1.13} 4p_x^{0.03} 3d_{yz}^{1.13} 4p_y^{0.03} 3d_{x^2-y^2}^{1.00} 3d_{xy}^{1.98} /$$

$$2s^{2.00} 2p_z^{1.06} 2p_x^{0.84} 2p_y^{0.84}.$$



The bonding can be attributed to a triple bond, two weak π bonds ($3d_{\pi}^{\text{Fe}} - 2p_{x,y}^{\text{C}}$) and one σ bond; the latter is caused by the coupling into a singlet of the $3d_{z^2}^{\text{Fe}} + 2p_z^{\text{C}}$ distributions, the “bonding” 3σ natural CASSCF orbital being $3\sigma \approx (0.76)4s^{\text{Fe}} + (0.49)2p_z^{\text{C}}$. According to Table II, the

recommended dissociation energy of FeC^- is $D_0^0(D_0^0) = 86 \pm 1 (84 \pm 1)$ kcal/mol at $r_e = 1.600 \text{ \AA}$ (C-MRCI + DKH8 + Q) to 1.604 \AA (C-ACPF + DKH8). Finally, the adiabatic electron affinity (EA) calculated at the C-ACPF + DKH8 level is $\text{EA} = 1.15 \text{ eV}$, very similar to the $\text{EA}(\text{C})$ of the C atom, $\text{EA}_{\text{expt}}(\text{C}) = 1.2621 \text{ eV}$.²²

The main conclusion of this short communication is that at the highest level of theory the binding energies (recommended values) of the ground states of $\text{FeC}(X^3\Delta)$, $\text{FeC}^+(X^2\Delta)$, and $\text{FeC}^-(X^2\Delta)$ are $D_0^0 = 87 \pm 1$, 95.2, and 84 ± 1 kcal/mol at $r_e = 1.581$, 1.556, and 1.600 \AA , respectively. The bonding similarity of the X-states of FeC ,¹ FeC^+ ,³ and FeC^- is reflected to the similarity of their bond energies and bond lengths. Notice that for both FeC and FeC^+ , there is no accurate experimental dissociation energy, whereas for FeC^- , this is the first *ab initio* calculation; therefore, reliable results for this species are reported for the first time.

ACKNOWLEDGMENTS

D.T. acknowledges financial support from the EU FP7, Capacities Program, NANOHOST project (Grant No. GA 201729) and the NATO (Grant No. CBP.MD.CLG.983711).

- ¹D. Tzeli and A. Mavridis, *J. Chem. Phys.* **116**, 4901 (2002).
- ²D. Tzeli and A. Mavridis, *J. Chem. Phys.* **118**, 4984 (2003); **122**, 056101 (2005).
- ³D. Tzeli and A. Mavridis, *J. Phys. Chem. A* **109**, 9249 (2005).
- ⁴K.-C. Lau, Y.-C. Chang, C.-S. Lam, and C. Y. Ng, *J. Phys. Chem. A* **113**, 14321 (2009).
- ⁵W. I. Balfour, J. Cao, C. V. V. Prasad, and C. X. W. Qian, *J. Chem. Phys.* **103**, 4046 (1995); M. D. Allen, J. C. Pesch, and L. M. Ziurys, *Astrophys. J. Lett.* **472**, L57 (1996).
- ⁶K. Aiuchi, K. Tsuji, and K. Shibuya, *Chem. Phys. Lett.* **309**, 229 (1999).
- ⁷T. C. Steimle, W. L. Virgo, and D. A. Hostutler, *J. Chem. Phys.* **117**, 1511 (2002).
- ⁸M. Fujitake, A. Toba, M. Mori, F. Miyazawa, N. Ohashi, K. Aiuchi, and K. Shibuya, *J. Mol. Spectrosc.* **208**, 253 (2001).
- ⁹Y.-C. Chang, C.-S. Lam, B. Reed, K.-C. Lau, H.-T. Lion, and C. Y. Ng, *J. Phys. Chem. A* **113**, 4242 (2009).
- ¹⁰R. L. Hettich and B. S. Freiser, *J. Am. Chem. Soc.* **108**, 2537 (1986).
- ¹¹C. Angeli, G. Berthier, C. Rolando, M. Sablier, C. Alcaraz, and O. Duttuit, *J. Phys. Chem. A* **101**, 7907 (1997).
- ¹²D. J. Brugh and M. D. Morse, *J. Chem. Phys.* **107**, 9772 (1997).
- ¹³E. F. Worden, B. Comaskey, J. Densberger, J. Christensen, J. M. McAfee, and J. A. Paisner, *J. Opt. Soc. Am. B* **1**, 314 (1984).
- ¹⁴G. L. Gutsev, L. Andrews, and C. W. Bauschlicher, Jr., *Theor. Chem. Acc.* **109**, 298 (2003); P. Redondo, L. Largo, and C. Barrientos, *Chem. Phys.* **364**, 1 (2009).
- ¹⁵N. B. Balabanov and K. A. Peterson, *J. Chem. Phys.* **123**, 064107 (2005).
- ¹⁶T. H. Dunning, Jr., *J. Chem. Phys.* **90**, 1007 (1989); D. Woon and T. H. Dunning, Jr., *ibid.* **103**, 4572 (1995).
- ¹⁷M. Douglas and N. M. Kroll, *Ann. Phys.* **82**, 89 (1974).
- ¹⁸B. A. Hess, *Phys. Rev. A* **32**, 756 (1985); **33**, 3742 (1986); G. Jansen and B. A. Hess, *ibid.* **39**, 6016 (1989).
- ¹⁹S. R. Langhoff and E. R. Davidson, *Int. J. Quantum Chem.* **8**, 61 (1974); E. R. Davidson and D. W. Silver, *Chem. Phys. Lett.* **52**, 403 (1977).
- ²⁰R. J. Gdanitz and R. Ahlrichs, *Chem. Phys. Lett.* **143**, 413 (1988); H. J. Werner and P. J. Knowles, *Theor. Chim. Acta* **78**, 175 (1990).
- ²¹MOLPRO, version 2006.1, a package of *ab initio* programs written by H.-J. Werner, P. J. Knowles R. Lindh *et al.*
- ²²M. Scheer, R. C. Bilodeau, C. A. Brodie, and H. K. Haugen, *Phys. Rev. A* **58**, 2844 (1998).