

**Comment on “Two isomers of SF• 5 and SF+ 5: Structures and energetics” [J. Chem. Phys. 100, 1759 (1994)]**

YuSan Cheung, WaiKee Li, SeeWing Chiu, and C. Y. Ng

Citation: *The Journal of Chemical Physics* **101**, 3412 (1994); doi: 10.1063/1.467591

View online: <http://dx.doi.org/10.1063/1.467591>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/101/4?ver=pdfcov>

Published by the [AIP Publishing](#)

---

**Articles you may be interested in**

Comment on “Thermodynamics of fluids in quenched disordered matrices” [J. Chem. Phys. 100, 5172 (1994)]

J. Chem. Phys. **102**, 5572 (1995); 10.1063/1.469287

Comment on “Integral equation theory for charged liquids: The structure of macroions in solution and the inversion of experimental data” [J. Chem. Phys. 100, 2244 (1994)]

J. Chem. Phys. **102**, 3486 (1995); 10.1063/1.468574

Comment on “Adsorption kinetics on chemically modified or bimetallic surfaces” [J. Chem. Phys. 100, 664 (1994)]

J. Chem. Phys. **101**, 11086 (1994); 10.1063/1.467798

Response to “Comment on ‘The weakest bond: Experimental observation of helium dimer’ ” [J. Chem. Phys. 100, 4021 (1994)]

J. Chem. Phys. **100**, 4023 (1994); 10.1063/1.466339

Two isomers of SF• 5 and SF+ 5: Structures and energetics

J. Chem. Phys. **100**, 1759 (1994); 10.1063/1.466603

---



# Comment on "Two isomers of SF<sub>5</sub><sup>+</sup> and SF<sub>5</sub><sup>+</sup>: Structures and energetics" [J. Chem. Phys. 100, 1759 (1994)]

Yu-San Cheung and Wai-Kee Li

Department of Chemistry, The Chinese University of Hong Kong, Shatin, N. T., Hong Kong

See-Wing Chiu

Biotechnology Center, University of Illinois, Urbana, Illinois 61801 and National Center for Supercomputing Applications, University of Illinois, Champaign, Illinois 61820

C. Y. Ng

Ames Laboratory,<sup>a)</sup> USDOE and Department of Chemistry, Iowa State University, Ames, Iowa 50011

(Received 11 March 1994; accepted 27 April 1994)

In a recent paper,<sup>1</sup> Becker *et al.* report experimental evidence<sup>2</sup> based on the chemical reactivities of SF<sub>5</sub><sup>+</sup> and results of *ab initio* quantum chemical calculations, which support the existence of two isomers with C<sub>4v</sub> and D<sub>3h</sub> symmetries for both SF<sub>5</sub> and SF<sub>5</sub><sup>+</sup>. Their calculations show that the most stable structures for SF<sub>5</sub> and SF<sub>5</sub><sup>+</sup> correspond to a distorted square pyramidal (C<sub>4v</sub>) and a trigonal bipyramidal (D<sub>3h</sub>) geometries, respectively, in accordance with predictions of the simple valence-shell-electron-pair repulsion theory<sup>3</sup> and the recent discrete-variation density calculation of Gutsev.<sup>4</sup> The theoretical findings of the higher energy isomers, SF<sub>5</sub>(D<sub>3h</sub>) and SF<sub>5</sub><sup>+</sup>(C<sub>4v</sub>), are used to reinterpret the previous conflicting experimental results for this system.<sup>5</sup>

In order to shed light on the energetics of SF<sub>5</sub> and SF<sub>5</sub><sup>+</sup>, we have performed *ab initio* quantum chemical calculations on this system using the Gaussian-2 (G2) procedure.<sup>6</sup> The G2 theory has been found to yield molecular energies predictions, such as bond dissociation energies (D<sub>0</sub>), adiabatic ionization energies (IE), and heats of formation at 0 K (ΔH<sub>f0</sub><sup>0</sup>), accurate to ±0.15 eV for molecular species consisting of the first- and second-row elements.<sup>6-15</sup> At the G2 level of theory, molecular structures are optimized using the second-order Møller-Plesset (MP2) perturbation calculations with a 6-31 G(d) basis set<sup>16</sup> and with all electrons included. The G2 method is an approximation of a QCISDT(T)/6-311+G(3df,2p) calculation and requires basis-set-extension energy corrections up to the MP4 level.

More recently, Curtiss *et al.* have introduced two variations of the G2 theory at reduced MP orders.<sup>17</sup> That version, which requires basis-set-extension energy corrections obtained at the second order, is referred to as the G2(MP2) theories. The G2(MP2) procedure gives slightly poorer results but involves significantly less computational time and disk storage than the G2 theory does. We have compared the experimental and theoretical G2 and G2(MP2) predictions for ΔH<sub>f0</sub><sup>0</sup>'s and adiabatic IEs of polyatomic species, such as CH<sub>3</sub>SS (Ref. 18), CH<sub>3</sub>CH<sub>2</sub>S (Ref. 15), and CH<sub>3</sub>SSCH<sub>3</sub> (Ref. 12). In all cases, the predictions based on the G2 and G2(MP2) are in good accord. The deviations between the

experimental and G2 and G2(MP2) results are less than ±0.2 eV. Due to the relatively large size of the molecular species of interest here, all calculations are only performed at the G2(MP2) level. The MP2/6-31G(d) harmonic frequencies, scaled by 0.93, are used to correct the zero-point vibrational energy (ZPVE). The total energy at 0 K (E<sub>0</sub>) is equal to E<sub>e</sub>+ZPVE, where E<sub>e</sub> is the total electronic energy. All calculations have been carried out on an IBM RS6000-340 workstation and CRAY-YMP using the GAUSSIAN 92 package of program.<sup>19</sup>

The geometry optimizations for SF<sub>5</sub> and SF<sub>5</sub><sup>+</sup> at both the HF/6-31(d) and MP2/6-31G(d) levels show that the SF<sub>5</sub>(C<sub>4v</sub>) and SF<sub>5</sub><sup>+</sup>(D<sub>3h</sub>) structures are true local minima, as reported in Ref. 1. However, the SF<sub>5</sub><sup>+</sup>(C<sub>4v</sub>) and SF<sub>5</sub>(D<sub>3h</sub>) structures have one and two imaginary vibrational frequencies, respectively, at the MP2/6-31G(d) level, and one and three imaginary vibrational frequencies, respectively, at the HF/6-31G(d) level, indicating that these structures are not local minima. This observation is contrary to the finding of Ref. 1.

Table I summarizes the E<sub>0</sub>, ΔH<sub>f0</sub><sup>0</sup>, and IE values obtained at the G2(MP2) level and compares them with currently recommended experimental ΔH<sub>f0</sub><sup>0</sup> and IE values for SF<sub>5</sub>(C<sub>4v</sub>) and SF<sub>5</sub><sup>+</sup>(D<sub>3h</sub>). The adiabatic IE for SF<sub>5</sub>(C<sub>4v</sub>)→SF<sub>5</sub><sup>+</sup>(D<sub>3h</sub>), calculated as the difference in E<sub>0</sub> values of SF<sub>5</sub>(C<sub>4v</sub>) and SF<sub>5</sub><sup>+</sup>(D<sub>3h</sub>), is 9.63 eV, in excellent agreement with the recent IE(SF<sub>5</sub>)=9.60±0.05 eV obtained by charge transfer bracketing techniques.<sup>5,20</sup> The theoretical ΔH<sub>f0</sub><sup>0</sup>[SF<sub>5</sub>(C<sub>4v</sub>)] is however, 14 kcal/mol lower than the recommended experimental value. This discrepancy is also the main cause of the difference observed between the experimental and theoretical ΔH<sub>f0</sub><sup>0</sup>[SF<sub>5</sub><sup>+</sup>(D<sub>3h</sub>)] values because ΔH<sub>f0</sub><sup>0</sup>[SF<sub>5</sub><sup>+</sup>(D<sub>3h</sub>)] is calculated as the sum of ΔH<sub>f0</sub><sup>0</sup>[SF<sub>5</sub>(C<sub>4v</sub>)] and IE[SF<sub>5</sub>(C<sub>4v</sub>)].

The accuracy in the application of G2(MP2) for molecular energy predictions of relatively large species, such as SF<sub>5</sub> and SF<sub>5</sub><sup>+</sup>, requires experimental confirmation. Since the experimental ΔH<sub>f0</sub><sup>0</sup> values for SF<sub>4</sub>, SF<sub>4</sub><sup>+</sup>, and SF<sub>6</sub> are well known, we have also performed G2(MP2) calculations on these species. As shown in Table I, the experimental and theoretical ΔH<sub>f0</sub><sup>0</sup> values for SF<sub>4</sub>, SF<sub>4</sub><sup>+</sup>, and SF<sub>6</sub> agree to within ±2 kcal/mol. The IE[G2(MP2)] of 11.85 eV for SF<sub>4</sub> is also in good accord with the value of 12.03±0.05 eV

<sup>a)</sup>Ames Laboratory is operated for the U. S. Department of Energy by Iowa State University under Contract No. W-7405-Eng-82. This article was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences.

TABLE I.  $E_0$ ,  $\Delta H_{f0}^0$ , and IE values obtained at the G2(MP2) level and current recommended experimental  $\Delta H_{f0}^0$  [ $\Delta H_{f0}^0(\text{exp})$ ] and IE [IE(exp)] for  $\text{SF}_4$ ,  $\text{SF}_4^+$ ,  $\text{SF}_5$ ,  $\text{SF}_5^+$ , and  $\text{SF}_6$ .

Species	$E_0[\text{G2(MP2)}]$ (hartree)	$\Delta H_{f0}[\text{G2(MP2)}]^a$ (kcal/mol)	$\Delta H_{f0}(\text{exp})^b$ (kcal/mol)	IE[G2(MP2)] <sup>c</sup> (eV)	IE(exp) (eV)
$\text{SF}_4(\text{C}_{2v})$	-796.675 66	-182.2	-182.3±3.7 -181±5 <sup>d</sup>	11.85	11.69±0.06 <sup>b</sup> 12.03±0.05 <sup>d</sup>
$\text{SF}_5(\text{C}_{4v})$	-896.365 30	-201.8	-221.8±4.3 -215.7±3.2 <sup>e</sup> -205.9±3.4 <sup>g</sup>	9.63	9.60±0.05 <sup>f</sup>
$\text{SF}_6(\text{O}_h)$	-996.164 57	-290.2	-288.4±0.2 <sup>d</sup>	...	15.33±0.03 <sup>d</sup>
$\text{SF}_4^+(\text{C}_{2v})$	-796.240 09	91.1	87.2±3.4 96.7±5.0 <sup>d</sup>	...	...
$\text{SF}_5^+(\text{D}_{3h})$	-896.011 41	20.3	-0.4±4.1 5.6±3.5 <sup>f</sup> 16.4±3.6 <sup>h</sup>	...	...

<sup>a</sup>Calculated using the  $E_0[\text{G2(MP2)}]$  values for species shown in the table, the  $E_0(\text{G2})$  values for S and F given in Ref. 17, and the known  $\Delta H_{f0}$  values for S (65.6±0.1 kcal/mol) and F(18.5±0.1 kcal/mol) given in Ref. 21.

<sup>b</sup>Unless specified, values are from Ref. 5.

<sup>c</sup>The IEs are calculated as the differences between the  $E_0$  values for the corresponding cationic and neutral species.

<sup>d</sup>Reference 21.

<sup>e</sup>Reference 22.

<sup>f</sup>Reference 20.

<sup>g</sup>Value calculated using the experimental  $D_0^0(\text{SF}_5-\text{F})=101$  kcal/mol (Ref. 22).

<sup>h</sup>Value calculated using the experimental  $D_0^0(\text{SF}_5-\text{F})=101$  kcal/mol (Ref. 22) and IE( $\text{SF}_5$ )=9.60±0.05 eV (Ref. 20).

recommended by Lias *et al.*,<sup>21</sup> and with the value of 11.69 ±0.06 eV obtained recently by Armentrout and co-workers.<sup>5</sup> The good agreement observed between the G2(MP2) and experimental IE and  $\Delta H_{f0}^0$  values supports that the G2(MP2) predictions for  $\text{SF}_5$  and  $\text{SF}_5^+$  should be reliable.

The experimental  $\Delta H_{f0}^0(\text{SF}_5)=-215\pm3.2$  kcal/mol is based on the upper limit of 91.1±3.2 kcal/mol for  $D_0^0(\text{SF}_5-\text{F})$  obtained by Kiang and Zare<sup>22</sup> in the study of the chemiluminescent reaction  $\text{SF}_6+\text{Sr}(^3P)$ . In the same experiment, an upper limit of 101.0±3.4 kcal/mol was obtained for  $D_0^0(\text{SF}_5-\text{F})$  by the  $\text{SF}_6+\text{Ca}(^3P)$  reaction. No logical arguments were given for the rejection of the  $\text{SF}_6+\text{Ca}(^3P)$  results. Interestingly, the latter limit is close to the G2(MP2) predictions of 106.9 kcal/mol for  $D_0^0(\text{SF}_5-\text{F})$ . The experimental  $D_0^0(\text{SF}_5-\text{F})=101$  kcal/mol translates to a value of -205.9±3.4 kcal/mol for  $\Delta H_{f0}^0(\text{SF}_5)$ , which agrees with the G2(MP2) prediction of -201.8 kcal/mol after taking the experimental uncertainty into account. Combining  $\Delta H_{f0}^0(\text{SF}_5)=-205.9\pm3.4$  kcal/mol and IE( $\text{SF}_5$ )=9.60±0.05 eV (Ref. 19), we calculate a value of 16.4±3.6 kcal/mol for  $\Delta H_{f0}^0(\text{SF}_5^+)$ , which is also in accord with the G2(MP2) prediction 20.3 kcal/mol.

Y. S. C. and W. K. L. are thankful for the support of a Hong Kong University and Polytechnic Grants Committee earmarked grant for research (Grant No. 221600080). C. Y. N. acknowledges the Donors of the Petroleum Research Fund, administered by the American Chemical Society, for the partial support of this research.

<sup>2</sup>G. Javahery, H. Becker, M. V. Korobov, M. Farber, D. Cooper, and D. K. Bohme, *Int. J. Mass Spectrom. Ion Processes* (in press).

<sup>3</sup>R. J. Gillespie and I. Hargittai, *The VSEPR Model of Molecular Geometry* (Allyn and Bacon, Needham Heights, 1991).

<sup>4</sup>G. L. Gutsev, *Russ. J. Inorg. Chem.* **37**, 135 (1992).

<sup>5</sup>E. R. Fisher, B. L. Kickel, and P. B. Armentrout, *J. Chem. Phys.* **97**, 4859 (1992); and references therein.

<sup>6</sup>L. A. Curtiss, K. Raghavachari, G. W. Trucks, and J. A. Pople, *J. Chem. Phys.* **94**, 7221 (1991).

<sup>7</sup>N. L. Ma, B. J. Smith, J. A. Pople, and L. Radom, *J. Am. Chem. Soc.* **113**, 7903 (1991).

<sup>8</sup>R. H. Nobes and L. Radom, *Chem. Phys. Lett.* **189**, 554 (1992).

<sup>9</sup>L. A. Curtiss, R. H. Nobes, J. A. Pople, and L. Radom, *J. Chem. Phys.* **97**, 6766 (1992).

<sup>10</sup>S.-W. Chiu, W.-K. Li, W.-B. Tzeng, and C. Y. Ng, *J. Chem. Phys.* **97**, 6557 (1992).

<sup>11</sup>N. L. Ma, W.-K. Li, and C. Y. Ng, *J. Chem. Phys.* **99**, 3617 (1993).

<sup>12</sup>W.-K. Li, S.-W. Chiu, and C. Y. Ng, *J. Chem. Phys.* **99**, 8840 (1993).

<sup>13</sup>N. L. Ma, W.-K. Li, D. P. Chong, and C. Y. Ng, *Chem. Phys.* **179**, 365 (1994).

<sup>14</sup>Z.-X. Ma, C.-L. Liao, C. Y. Ng, Y.-S. Cheung, W.-K. Li, and T. Baer, *J. Chem. Phys.* **100**, 4780 (1994).

<sup>15</sup>Z.-X. Ma, C.-L. Liao, H.-M. Yin, C. Y. Ng, S.-W. Chiu, N.-L. Ma, and W.-K. Li, *Chem. Phys. Lett.* **213**, 250 (1993).

<sup>16</sup>W. J. Hehre, L. Radom, P. v. R. Schleyer, and J. A. Pople, *Ab Initio Molecular Orbital Theory* (Wiley, New York, 1986).

<sup>17</sup>L. A. Curtiss, K. Raghavachari, and J. A. Pople, *J. Chem. Phys.* **98**, 1293 (1993).

<sup>18</sup>Y.-S. Cheung, W. K. Li, and C. Y. Ng, to be published.

<sup>19</sup>M. J. Frisch *et al.*, GAUSSIAN 90 (Gaussian Inc., Pittsburg, PA, 1990); GAUSSIAN 92 (Gaussian Inc., Pittsburgh, PA, 1992).

<sup>20</sup>L. W. Sieck and P. J. Ausloos, *J. Chem. Phys.* **93**, 8374 (1990).

<sup>21</sup>S. G. Lias, J. E. Bartmess, J. F. Liebman, J. L. Holmes, R. D. Levin, and W. G. Mallard, *J. Phys. Chem. Ref. Data* **17**, Suppl. 1 (1988).

<sup>22</sup>T. Kiang and R. N. Zare, *J. Am. Chem. Soc.* **102**, 4024 (1980).

<sup>1</sup>H. Becker, J. Hrušák, H. Schwarz, and D. K. Bohme, *J. Chem. Phys.* **100**, 1759 (1994).