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The fluoride affinity of SO_2

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Dedicated on the occasion of his 60th birthday to Jack Beauchamp, in appreciation of his many contributions to the study of ion chemistry.

Abstract

Energy-resolved collision-induced dissociation (CID) experiments using a flowing afterglow-tandem mass spectrometer (MS) have been performed on SO_2F^-. The results give a 298 K bond enthalpy of $D(SO_2–F^-) = 225 \pm 9\,kJ\,mol^{-1}$. G3/B3LYP and G3(MP2) calculations give corresponding values of 215 and 217 $kJ\,mol^{-1}$, in reasonable agreement with the experimental results. The experimental result is 42 $kJ\,mol^{-1}$ higher than results previously reported using ion cyclotron resonance (ICR) equilibrium techniques, but is in good agreement with relative values. (Int J Mass Spectrom 222 (2003) 221–227)

Keywords: Fluoride affinity; Thermodynamics; CID; Ab initio calculations

1. Introduction

Sulfur dioxide is an important non-aqueous solvent [1,2]. SO_2 can act as a Lewis acid and accept halide ligands to form halosulfite anions ($XSO_2{}^-$). Salts such as KSO_2F are mild fluorinating agents [2,3]. Spectroscopic [4,5] and calorimetric [6] methods have been used to determine bond energies in solution for halosulfite anions. However, these techniques have not been applied to SO_2F^- because the S–F bond is sufficiently strong to make it impossible to measure the equilibrium constant for dissociation [4].

Halosulfite anions have also been observed in the gas phase [7]. SF_6 is a key component of industrial plasmas, and is becoming a more significant trace species in the atmosphere [8–10]. The fluorosulfite anion is observed in SF_6 plasmas in the presence of water, a common contaminant [10]. Thus, understanding the thermodynamics of halosulfites may clarify reaction chemistry of current interest.

Beauchamp and coworkers performed pioneering studies of fluoride affinities (FAs) using ion cyclotron resonance (ICR) bracketing techniques [11–13]. They noted that SO_2F^- transfers fluoride to HF [13]; assuming that the reaction is therefore exothermic means that $FA(SO_2) \leq FA(HF) = 192 \pm 7\,kJ\,mol^{-1}$ [23]. However, Larson and McMahon (LM) have suggested that the reactivity observed in the earlier experiments may be due to excited states of SO_2F^-, [14] which would make the upper limit invalid.

LM included SO_2F^- in their extensive FA ladder [14,15], reporting $FA(SO_2) = 183\,kJ\,mol^{-1}$. This affinity ladder [16,17] is formed by determining a series of relative FAs using fluoride transfer equilibrium constant measurements in an ICR, and then anchoring the ladder with a reference value of $FA(H_2O) =$

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97.5 kJ mol^{-1} [18]. The LM scale is still one of the major sources of fluoride affinity values [19].

Recent high pressure mass spectrometry (HPMS) measurements by McMahon and coworkers [20] give values for the FA of ethanol, isopropanol, and *tert*-butanol that are within the experimental uncertainties of the values previously reported [15]. DeTuri and Ervin [21] have determined these same three values by measuring thresholds for collision-induced dissociation (CID) of ROH–F$^-$ clusters; the results are in excellent agreement with the recent HPMS values. Hiraoka et al. [22] obtained a value for FA(CO_2) essentially identical to the LM value [15]. The alcohols and CO_2 all have FAs in the 130–140 kJ mol^{-1} range (near the middle of the FA scale), and these results indicate that there are no systematic problems with the FA scale in this region.

In the higher part of the FA scale, two subsequent measurements give FA(HF) $= 192 \pm 7$ kJ mol^{-1} [23] and FA(SF_4) $= 232 \pm 10$ kJ mol^{-1} [24], values that are 31 and 49 kJ mol^{-1} higher than those given by LM. The result for SF_4 is particularly relevant to the present study because LM found FA(SO_2) and FA(SF_4) to be identical within the small experimental uncertainty for measurement of a single equilibrium constant [15]. Squires reported a preliminary SO_2–F$^-$ bond strength of 222 ± 10 kJ mol^{-1} [25], 39 kJ mol^{-1} higher than the value reported by LM. Wenthold and Squires also noted that other experiments imply that the best value for FA(CH_2CO) is 38 kJ mol^{-1} higher than the LM value [23]. Thus, it is clear that the original FA scale needs adjusting over at least part of its range; one purpose of this project is to further test the fluoride affinity scale.

Near the bottom of the FA scale, FA(H_2O) has been recently revised from 97.5 kJ mol^{-1} [18] to 109.6 ± 3.3 kJ mol^{-1} [26]. FA(H_2O) $=$ 110.9 kJ mol^{-1} has also been calculated [26,27] at high levels of theory. This 12 kJ mol^{-1} discrepancy, however, is significantly smaller than the possible changes in the higher end of the scale.

New absolute measurements of FAs can allow local regions of the relative fluoride affinity scale to be used with confidence. For example, Huey et al. [28] used the revised value for FA(SO_2) [25] and a single step on the fluoride affinity ladder [14], FA(SO_2) $=$ FA(COF_2) $+$ 5 kJ mol^{-1}, to derive FA(COF_2) $= 217 \pm 11$ kJ mol^{-1}; improvement in the precision of FA(SO_2) will improve the precision of FA(COF_2).

Anions such as SO_2F^- are also good tests for computational methods [29]. An advantage of SO_2F^- is that it is relatively small, making high-level calculations possible without the use of large amounts of computer time. Previous calculations of the bond energy by Maulitz et al. [30] using techniques up to MP4SDQ/6-31+G(3df)//MP2/6-31+G(3df) and QCISD(T)/6-31+G(3df)//MP2/6-31+G(3df), and by Arnold et al. [10] using G2 methods, are compared below to the experimental results and to new calculations using the G3/B3LYP and G3(MP2) methods.

2. Experimental

The bond activation energy in SO_2F^- was measured using the energy-resolved CID technique [31] in a flowing afterglow-tandem mass spectrometer (MS) [32]. The instrument, a second-generation development of a device built by Armentrout and Beauchamp [33], consists of an ion source region, a flow tube, and the tandem MS. The dc discharge ion source used in these experiments is typically set at 1.5 mA of emission current. The flow tube is a 92 cm × 7.3 cm i.d. stainless steel pipe that operates at a buffer gas pressure of 0.4 Torr with a flow rate of 200 standard cm^3 s^{-1}. The buffer gas is helium with up to 10% argon added to stabilize the dc discharge.

To make the ions for this study, the gases SF_6 and SO_2 were added to the ion source at a low flow rate. SF_6 undergoes dissociative electron capture to produce F$^-$, and addition of this ion to SO_2 produces the desired adduct, SO_2F^-. Approximately 10^5 collisions with the buffer gas cool the metastable adduct ions to room temperature.

The tandem MS includes a quadrupole mass filter, an octopole ion guide, a second quadrupole mass filter, and a detector, contained in a stainless steel box that is partitioned into five interior chambers.

Differential pumping on the five chambers ensures that further collisions of the ions with the buffer gas are unlikely after ion extraction. During CID experiments, the SO_2F^- ions are extracted from the flow tube and focused into the first quadrupole for mass selection. The reactant ions are then focused into the octopole, which passes through a reaction cell that contains Ar collision gas. After the dissociated and unreacted ions pass through the reaction cell, the second quadrupole is used for mass analysis. The detector is an electron multiplier operating in pulse-counting mode.

The energy threshold for CID is determined by modeling the cross-section for product formation as a function of the reactant ion kinetic energy in the center-of-mass (CM) frame, E_{cm}. The octopole is used as a retarding field analyzer to measure the reactant ion beam energy zero. The ion kinetic energy distribution is approximately Gaussian with a full-width at half-maximum of 1.1 ± 0.2 eV (1 eV $=$ 96.5 kJ mol^{-1}). The octopole offset voltage measured with respect to the center of the Gaussian fit gives the laboratory kinetic energy, E_{lab} in eV. Low offset energies are corrected for truncation of the ion beam [34]. To convert to the CM frame, the equation $E_{cm} = E_{lab} m (m + M)^{-1}$ is used, where m and M are the masses of the neutral and ionic reactants, respectively. All experiments were performed with both mass filters at low resolution to improve ion collection efficiency and reduce mass discrimination.

The total cross-section for a reaction, σ_{total}, is calculated using Eq. (1), where I is the intensity of the reactant ion beam, I_0 the intensity of the incoming beam ($I_0 = I + \sum I_i$), I_i the intensity of each product ion, n the number density of the collision gas, and l is the effective collision length, 13 ± 2 cm. Individual product cross-sections σ_i are equal to $\sigma_{total}\ (I_i / \sum I_i)$.

$$I = I_0 \exp(-\sigma_{total} n l) \tag{1}$$

Threshold energies are derived by fitting the data to a model function given in Eq. (2), where $\sigma(E)$ is the cross-section for formation of the product ion at CM energy E, E_T the desired threshold energy, σ_0 the scaling factor, n an adjustable parameter, and i denotes rovibrational states having energy E_i and population g_i ($\sum g_i = 1$). Doppler broadening and the kinetic energy distribution of the reactant ion are also accounted for in the data analysis, which is done using the CRUNCH program written by Armentrout and coworkers [34].

$$\sigma(E) = \frac{\sigma_0 \sum g_i (E + E_i - E_T)^n}{E} \tag{2}$$

Collisionally activated metastable complexes can have sufficiently long lifetimes that they do not dissociate on the experimental timescale (ca. 50 μs). Such kinetic shifts are accounted for in the CRUNCH program by RRKM lifetime calculations. SO_2F^- has a negligible kinetic shift, <0.1 kJ mol^{-1}.

Computational work on these systems was performed using the Gaussian'98 suite [35]. Several groups have previously calculated D(SO_2–F^-) using high-level computational techniques (Table 1). In addition, we examined these reactions using the G3(MP2) [36] and G3/B3LYP approaches [37] recently incorporated into the Gaussian'98 suite.

Vibrational and rotational constants and the polarizability of SO_2 were calculated using the B3LYP method and the 6-311+G(d) basis set. Schaefer and coworkers have performed extensive tests of the applicability of various computational methods to anions; they found that the B3LYP method gives good results for the computational cost, although somewhat larger basis sets give better energetics [29]. The calculated and known experimental values are given in

Table 1
Comparison of SO_2–F^- bond enthalpies[a]

Method	Value	Reference
ICR bracketing	≤192 ± 7	[11]
ICR equilibrium	183	[15]
CID	222	[25]
CID	225 ± 9	This work
MP4SDQ/6-31+G(3df)//MP2/6-31+G(3df)	211	[30]
QCISD(T)/6-31+G(3df)/MP2/6-31+G(3df)	212	[30]
G2	218	[10]
G3(MP2)	220	This work
G3/B3LYP	217	This work

[a] 298 K values in kJ mol^{-1}.

Table 2
Molecular constants

Compound	Experimental vibration (cm^{-1})	Calculated vibration (cm^{-1})[a]	Rotation (cm^{-1})[a]	Polarizability (10^{-24} cm^3)[a]
SO_2F^- [39]	–	290	0.2959	5.30
	360	304	0.2331	
	471	467	0.1473	
	598	544		
	1100	1067		
	1178	1161		
SO_2 [38]	517	505	1.9071	3.43
	1147	1131	0.3348	
	1351	1311	0.2848	

[a] Present work, calculated at the B3LYP/6-311+G(d) level.

Table 2. The calculated frequencies for SO_2 are lower than the known experimental values [38] by less than 2.2 ± 0.8%. The optimized geometry for SO_2F^- is shown in Fig. 1.

The vibrational frequencies of several SO_2F^- salts have been measured in the solid state [3], and some of the frequencies have been measured using matrix isolation techniques [39]. The matrix frequency set is incomplete, and apparently the solid state frequencies are perturbed by the presence of other ions. Therefore, the calculated values are used in the data modeling (for consistency, the calculated values are also used for SO_2). Uncertainties in the derived thresholds due to possible inaccuracies in the frequencies were estimated by multiplying entire sets of frequencies for reactants, activated complexes, or transition states by 0.9 and 1.1. The resulting changes in internal energies were less than 0.5 kJ mol^{-1}. Other possible inaccuracies in transition state modeling were simulated by multiplying the time window for dissociation by 10 and 0.1. These variations change the derived thresholds by less than 0.1 kJ mol^{-1}. These uncertainties are included in the final uncertainties of the derived thresholds.

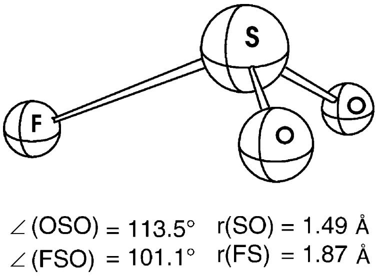

Fig. 1. Calculated geometry for SO_2F^- at the B3LYP/6-311+G(d) level.

An ion not sufficiently energized by one collision with the target gas may gain enough energy in a second collision to be above the dissociation threshold. This effect is eliminated by linear extrapolation of the data taken at several pressures to a zero pressure cross-section before fitting the data [40].

3. Results

CID of SO_2F^- gives loss of fluoride anion as the only detectable product (reaction 3). This is consistent with the relative electron affinities: $EA(F) = 3.401$ eV [41] and $EA(SO_2) = 1.107 \pm 0.008$ eV [42]. Representative data for formation of F^- is shown in Fig. 2. The Eq. (2) fitting parameters are $E_T = 2.35 \pm 0.07$ eV, $n = 1.38 \pm 0.14$, and $\sigma_0 = 2.19 \pm 0.74$. The fit to the data is shown in Fig. 2 as well. The dissociation thresholds correspond to the bond activation energy at 0 K, since the effects of reactant and product internal energy are included in the fitting procedure. The final uncertainty in the energy is derived from the standard deviation of the thresholds determined for individual datasets, the uncertainty in the reactant internal energy, the effects of kinetic shifts, and the uncertainty in the energy scale (±0.15 eV lab). This gives a final

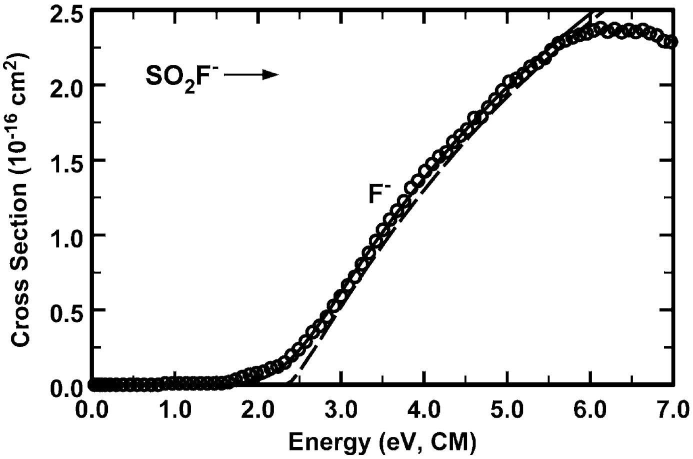

Fig. 2. Cross-section for collision-induced dissociation of SO_2F^- as a function of energy in the center-of-mass frame. The solid and dashed lines represent convoluted and unconvoluted fits to the data, as discussed in the text.

0 K value of $D(SO_2–F^-) = 227 \pm 9\,kJ\,mol^{-1}$.

$$SO_2F^- \rightarrow SO_2 + F^- \quad (3)$$

The 0 K bond energy can be converted to a bond enthalpy at 298 K of 225 ± 9 kJ mol^{-1} using the heat capacities of the reactants and products. The heat capacities are determined using the frequencies calculated at the B3LYP/6-311+G(d) level (Table 1). The 298 K bond enthalpy (the fluoride affinity) is the most commonly reported value in the previous literature, and so this value will be used in the following discussion.

We also calculated FA(SO_2) using the G3(MP2) [43] and G3/B3LYP [44] approaches. These models give absolute average deviations (AADs) from experiment for molecules within the G2 database of 0.056 and 0.043 eV, respectively, improvements over the AADs of 0.082 and 0.064 eV determined for the G2(MP2) and G2 approaches. The derived values are 217 and 215 kJ mol^{-1}, respectively.

4. Discussion

4.1. Comparison to previous work

The value for FA(SO_2) obtained in this work is 42 kJ mol^{-1} higher than the value obtained by LM. This is quite consistent with other studies noted in the introduction, which gave FA values for several molecules that are 31–49 kJ mol^{-1} higher than the LM scale. These molecules have FAs reported by LM [15] ranging from 148 to 183 kJ mol^{-1}. The discrepancy at the higher end of the scale, combined with the excellent agreement for the alcohols in 132–139 kJ mol^{-1} range, suggests that an error occurs in the fluoride affinity scale between these regions.

The present value of FA(SO_2) = 225 ± 9 kJ mol^{-1} is in excellent agreement with the preliminary value of 222±10 kJ mol^{-1} reported by Hop et al. [25]. The new work therefore has only a minor effect on the adjusted values for nearby FAs. For example, FA(COF_2) = 220 kJ mol^{-1} is close to the value used by Huey et al. [28]. LM reported identical FAs for SO_2 and SF_4; the present value for SO_2 is in good agreement with FA(SF_4) = 232 ± 10 kJ mol^{-1} reported recently [24].

Maulitz et al. [30] previously calculated $D(SO_2–F^-)$ using several methods and the 6-31+G(3df) basis set; the values at the MP4SDQ//MP2 and QCISD(T)//MP2 levels are 211 and 212 kJ mol^{-1}, respectively. Arnold et al. [10] calculated FA(SO_2) = 218 kJ mol^{-1} using the G2 method. These values and the G3 values calculated in this work are 5–14 kJ mol^{-1} below the new experimental value. Thus, several very high-level techniques give consistent results at roughly the bottom end of the experimental uncertainty. A comparatively moderate level B3LYP/6-311+G(d) calculation gives $\mathrm{FA(SO_2)} = 212\,\mathrm{kJ\,mol^{-1}}$, suggesting that the calculated value is not very dependent on the type of calculation. In contrast, extremely large basis sets are needed to give highly accurate results for the atomization energies of SO_2 and SO_3 [45].

The other halide affinities of SO_2 have also been measured. Caldwell and Kebarle derived $\mathrm{D(SO_2–X^-)} = 93$, 81, and $60\,\mathrm{kJ\,mol^{-1}}$ for X = Cl, Br, and I, respectively [46]. Two other groups determined similar values for $\mathrm{D(SO_2–Cl^-)}$ of 91 [47] and $87\,\mathrm{kJ\,mol^{-1}}$ [14]. It is typical for FAs to be more than twice as strong as chloride affinities [14], and the values for SO_2 are in accord with this. The trend in the full set of halide affinities correlates with the large difference between the electronegativities of fluorine and chlorine, and the much smaller differences between the electronegativities of chlorine, bromine, and iodine. Solvation effects reduce but do not eliminate the differences in the bond strengths in solution [4–6].

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References

[1] N.N. Greenwood, A. Earnshaw, Chemistry of the Elements, 2nd ed., Butterworth-Heinemann, Oxford, 1997.
[2] F.A. Cotton, G. Wilkinson, C.A. Murillo, M. Bochmann, Advanced Inorganic Chemistry, 6th ed., Wiley, New York, 1999.
[3] K.H. Moock, D. Sülzle, P. Klaeboe, J. Fluorine Chem. 47 (1990) 151.
[4] E.J. Woodhouse, T.H. Norris, Inorg. Chem. 10 (1971) 614.
[5] A. Salama, S.B. Salama, M. Sobeir, S. Wasif, J. Chem. Soc. A (1971) 1112;
S.B. Salama, S. Wasif, J. Chem. Soc., Dalton Trans. (1975) 151;
S.B. Salama, S. Wasif, M. M. Omer, J. Chem. Soc., Dalton Trans. (1978) 918.
[6] E. Milanova, R.L. Benoit, Can. J. Chem. 55 (1977) 2807.
[7] R.M. Reese, V.H. Dibeler, J.L. Franklin, J. Chem. Phys. 19 (1958) 880;
R. Robbiani, J.L. Franklin, J. Am. Chem. Soc. 101 (1979) 764.
[8] V. Tarnovsky, H. Deutsch, K.E. Martus, K. Becker, J. Chem. Phys. 109 (1998) 6596.
[9] C.L. Lugez, M.E. Jacox, R.A. King, H.F. Schaefer III, J. Chem. Phys. 108 (1998) 9639.
[10] S.T. Arnold, T.M. Miller, A.A. Viggiano, J. Phys. Chem. A (2002) 112, article ASAP.
[11] M.K. Murphy, J.L. Beauchamp, J. Am. Chem. Soc. 99 (1977) 4992.
[12] S.A. Sullivan, J.L. Beauchamp, Inorg. Chem. 17 (1978) 1589.
[13] S.A. Sullivan, J.L. Beauchamp, Int. J. Mass Spectrom. Ion Phys. 28 (1978) 69.
[14] J.W. Larson, T.B. McMahon, J. Am. Chem. Soc. 107 (1985) 766.
[15] J.W. Larson, T.B. McMahon, J. Am. Chem. Soc. 105 (1983) 2944;
J.W. Larson, T.B. McMahon, Inorg. Chem. 26 (1987) 4018.
[16] T.B. McMahon, Int. J. Mass Spectrom. 200 (2000) 187.
[17] K.O. Christe, D.A. Dixon, D. McLemore, W.W. Wilson, J.A. Sheehy, J.A. Boatz, J. Fluorine Chem. 101 (2000) 151.
[18] M. Arshadi, R. Yamdagni, P. Kebarle, J. Phys. Chem. 74 (1970) 1475.
[19] J.E. Bartmess, in: P.J. Linstrom, W.G. Mallard (Eds.), Negative Ion Energetics Data in NIST Chemistry WebBook, NIST Standard Reference Database Number 69, National Institute of Standards and Technology, Gaithersburg, MD, 2001 (http://webbook.nist.gov).
[20] B. Bogdanov, M. Peschke, D.S. Tonner, J.E. Szulejko, T.B. McMahon, Int. J. Mass Spectrom. 185 (1999) 707.
[21] V.F. DeTuri, K.M. Ervin, J. Phys. Chem. A 103 (1999) 6911.
[22] K. Hiraoka, S. Mizuse, S. Yamabe, J. Chem. Phys. 87 (1987) 3647.
[23] P.G. Wenthold, R.R. Squires, J. Phys. Chem. 99 (1995) 2002.
[24] K.C. Lobring, C.E. Check, T.M. Gilbert, L.S. Sunderlin, Int. J. Mass Spectrom., in press.
[25] C.E.C.A. Hop, T.B. McMahon, J.A. Paulino, R.R. Squires, unpublished work, cited in R.R. Squires, Int. J. Mass Spectrom. Ion Process. 117 (1992) 565.
[26] P. Weis, P.R. Kemper, M.T. Bowers, S.S. Xantheas, J. Am. Chem. Soc. 121 (1999) 3531.
[27] S.S. Xantheas, L.X. Dang, J. Phys. Chem. 100 (1996) 3989.
[28] L.G. Huey, E.J. Dunlea, C.J. Howard, J. Phys. Chem. 100 (1996) 6504.
[29] J.C. Rienstra-Kiracofe, G.S. Tschumper, H.F. Schaefer III, S. Nandi, G.B. Ellison, Chem. Rev. 102 (2002) 231.
[30] A.H. Maulitz, R. Boese, N. Kuhn, J. Mol. Struct. 333 (1995) 227.
[31] F. Muntean, P.B. Armentrout, J. Chem. Phys. 115 (2001) 1213 (and references therein).

[32] K. Do, T.P. Klein, C.A. Pommerening, L.S. Sunderlin, J. Am. Soc. Mass Spectrom. 8 (1997) 688.

[33] P.B. Armentrout, J.L. Beauchamp, Chem. Phys. 50 (1980) 21; P.B. Armentrout, J.L. Beauchamp, J. Chem. Phys. 74 (1981) 2819.

[34] K.M. Ervin, P.B. Armentrout, J. Chem. Phys. 83 (1985) 166; M.T. Rodgers, K.M. Ervin, P.B. Armentrout, J. Chem. Phys. 106 (1997) 4499.

[35] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery Jr., R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, A.D. Malick, K.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, A.G. Baboul, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, J.L. Andres, C. Gonzalez, M. Head-Gordon, E.S. Replogle, J.A. Pople, Gaussian'98, Revision A.9, Gaussian Inc., Pittsburgh, PA, 1998.

[36] L.A. Curtiss, P.C. Redfern, K. Raghavachari, V. Rassolov, J.A. Pople, J. Chem. Phys. 110 (1999) 4703.

[37] A.G. Baboul, L.A. Curtiss, P.C. Redfern, K. Raghavachari, J. Chem. Phys. 110 (1999) 7650.

[38] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, 5th ed., Part A, Wiley-Interscience, New York, 1997.

[39] K. Garber, B.S. Ault, Inorg. Chem. 22 (1983) 2509.

[40] S.K. Loh, D.A. Hales, L. Lian, P.B. Armentrout, J. Chem. Phys. 90 (1989) 5466;
R.H. Schultz, K.C. Crellin, P.B. Armentrout, J. Am. Chem. Soc. 113 (1991) 8590.

[41] C. Blondel, P. Cacciani, C. Delsart, R. Trainham, Phys. Rev. A 40 (1989) 3698.

[42] M.R. Nimlos, G.B. Ellison, J. Phys. Chem. 90 (1986) 2574.

[43] L.A. Curtiss, P.C. Redfern, K. Raghavachari, V. Rassolov, J.A. Pople, J. Chem. Phys. 110 (1999) 4703.

[44] A.G. Baboul, L.A. Curtiss, P.C. Redfern, K. Raghavachari, J. Chem. Phys. 110 (1999) 7650.

[45] J.M.L. Martin, J. Chem. Phys. 108 (1998) 2791;
J.M.L. Martin, Chem. Phys. Lett. 310 (1999) 271.

[46] G. Caldwell, P. Kebarle, Can. J. Chem. 63 (1985) 1399.

[47] R.G. Keesee, A.W. Castleman Jr., J. Am. Chem. Soc. 102 (1980) 1446;
R.G. Keesee, N. Lee, A.W. Castleman Jr., J. Chem. Phys. 73 (1980) 2195.