Two isomers of $SF_5^\bullet$ and SF_5^+: Structures and energetics

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The apparently conflicting results for the ionization energy of $SF_5^\bullet$ and the standard enthalpy of formation of SF_5^+ reported over the last 25 years have been reinterpreted and brought into line in terms of the existence of square pyramidal (C_{4v}) and trigonal bipyramidal (D_{3h}) isomers of $SF_5^\bullet$ and SF_5^+. New experimental results and theoretical calculations are reported which are consistent with this interpretation. Values are recommended for the ionization energy and standard enthalpies of formation for the two isomers of $SF_5^\bullet$ and SF_5^+.

The ionization energy of $SF_5^\bullet$, IE($SF_5^\bullet$), and the standard enthalpy of formation of SF_5^+, ΔH_f^0 (SF_5^+), have been the subject of many experimental investigations with apparently conflicting results for more than 25 years, as has recently been summarized in J. Chem. Phys. by Fisher, Kickel, and Armentrout.[1] It has been implicitly assumed in all of these studies that $SF_5^\bullet$ and SF_5^+ each have a single electronic structure. However, recent measurements in our laboratory of ion/molecule reactions with S_2F_{10} have revealed the production of two states of SF_5^+ with distinctly different chemical reactivities and we have proposed that these states correspond to square pyramidal (C_{4v}) and trigonal bipyramidal (D_{3h}) isomers.[2] Here we present results of theoretical calculations, as well as further experiments, which provide convincing evidence for the stabilities of these two isomers for both SF_5^+ and $SF_5^\bullet$ and which begin to bring into line the many, seemingly conflicting, results of previous measurements of IE ($SF_5^\bullet$) and ΔH_f^0 (SF_5^+).

With a view to the possible formation of two isomers of SF_5^+, an inspection of the experimental results summarized in Table I of Ref. 1 shows two sets of values for IE($SF_5^\bullet$) and $\Delta H^o_{f,0}$(SF_5^+): (six) values in the range 11.31 ± 0.2 to 11.9 ± 0.2 eV and 46 ± 1 to 60×5 kcal mol^{-1}, respectively, derived from appearance energy measurements with SF_6, and (four) values in the range 9.60 ± 0.05 to 9.83 ± 0.23 eV and 2.7 ± 4.4 kcal mol^{-1} (recommended),[1] respectively, derived from studies of ion/molecule reactions involving SF_5^+ derived from SF_6. The low value for IE($SF_5^\bullet$) derived from photoionization appearance energy (AE) measurements with SF_5Cl can be assigned to the preferred removal of a "lone pair" electron on Cl,[3] followed by intramolecular charge transfer and dissociation. The intermediate value of 10.6 eV derived from electron-impact AE measurements with SF_5Cl has been discounted on the basis of the energy spread of the ionizing electrons employed in these measurements.[4] Of the intermediate values, the upper limits of 10.0 and 10.4 eV for IE($SF_5^\bullet$) derived from the observation of ion/molecule reactions are consistent with the four low values, and the value of 10.02 ± 0.14 eV[5] can be discounted since it is based on the erroneous observation with the flowing afterglow (FA) technique of charge transfer between SF_5^+ and NH_3.[6] This latter reaction has been observed to proceed by HF elimination rather than charge transfer by others using other mass-spectrometry experiments.[7,8] We have investigated the same reaction in our selected-ion flow tube (SIFT) apparatus under conditions similar to the FA experiments and can report a fast reaction, $k = (1.0 \pm 0.3) \times 10^{-9}$ cm^3 $molecule^{-1}$ at 297 K, which leads primarily to HF elimination ($>97\%$) with trace amounts of F^+ transfer ($<2\%$) and adduct formation ($<1\%$), rather than charge transfer. The value of 10.67 ± 0.17 eV must also be discounted since it is based on FA equilibrium-constant measurements for the F^- transfer reaction between CF_3^+ and SF_6 which were discredited by high-pressure[8] and guided ion-beam[9] mass spectrometry measurements which did not support the attainment of equilibrium in this reaction.

We interpret the results in Table I of Ref. 1 to provide evidence for a high and a low ionization energy which we associate with the ionization of the C_{4v} isomer of SF_5 to yield the isomers SF_5^+ (C_{4v}) and SF_5^+ (D_{3h}), respectively. We propose that AE measurements with SF_6 produce the high-energy C_{4v} isomer of SF_5^+, while ion–molecule reactions produce the low-energy D_{3h} isomer.

Also, the (six) values for IE ($SF_5^\bullet$) in Table I of Ref. 1 need to be corrected downwards since their derivation from AE measurements with SF_6 did not recognize that the SF_5^+ produced in such measurements arises from the dissociation of ground-state $SF_6^{\bullet +}$ which lies *above* the thermochemical appearance energy of SF_5^+. Various experiments have shown that this dissociation releases 0.9 ± 0.1 eV of translational energy in the products $SF_5^+F^\bullet$, viz. the X state of $SF_6^{\bullet +}$ lies above the lowest dissociation channel yielding $SF_5^+ + F^\bullet$ and is a repulsive state.[10,11] This means that the (six) values for IE($SF_5^\bullet$) in Table I must be reduced by at least 0.9 ± 0.1 eV from the range 11.31 to 11.9 eV to the range 10.4 to 11.0 eV.

Theory is in accord with such an interpretation. Very recently Gutsev has shown, using a discrete-variation density method, that the ground states of SF_5^+ and $SF_5^\bullet$ have D_{3h} and C_{4v} symmetry, respectively.[12] It was not possible to establish whether the C_{4v} and D_{3h} configurations of the

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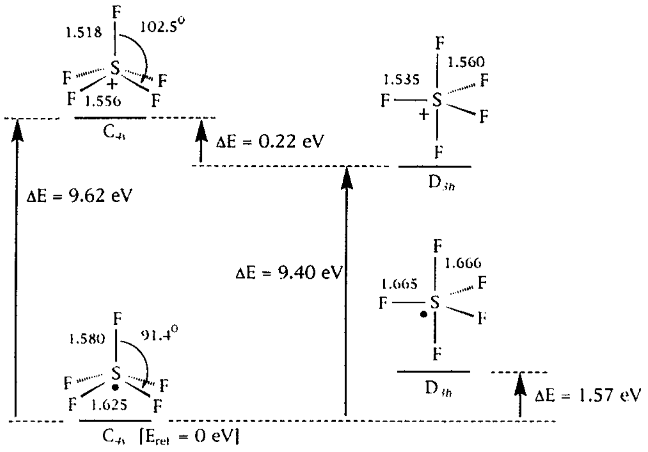

FIG. 1. Energies and bond lengths computed at the second-order MP2 level of theory using the 6–31G(d) basis set. The geometries have been optimized under the restriction of C_{4v} and D_{3h} symmetry, respectively. Gutsev has reported angles of 90.8° and 102.6° for $SF_5^\bullet$ (C_{4v}) and SF_5^+ (C_{4v}), respectively (Ref. 12).

cation and radical were local minima or transition states, but energy differences for the C_{4v} and D_{3h} configurations were reported to range from 0.19 to 0.27 eV for SF_5^+ and from 0.90 to 1.54 eV for $SF_5^\bullet$, respectively, depending on the method used.[12] Geometries and relative energies of the square pyramidal and trigonal bipyramidal isomers of $SF_5^\bullet$ and SF_5^+ computed in the present study are given in Fig. 1. The calculations of energies and fully optimized geometries were performed in the framework of second-order Møller–Plesset (MP2) theory with a polarized 6–31G(d) basis set.[13] All calculations were performed with the GAUSSIAN 90 program[14] using a CONVEX 230 computer. In agreement with Gutsev, the C_{4v} configuration was found to be the global minimum of $SF_5^\bullet$. The D_{3h} configuration was found to be a local minimum and to lie 1.57 eV higher in energy. This situation is reversed for the cation for which the D_{3h} isomer was found to be stabilized by 0.22 eV with respect to the C_{4v} configuration. The analysis of the force constant matrix demonstrates that all four species are true minima, and the relative stabilities found using the MP2 method compares well with the results of the density functional calculations reported previously by Gutsev.[12] The computed energies for the ionization of $SF_5^\bullet(C_{4v})$ to SF_5^+ (D_{3h}) and SF_5^+ (C_{4v}) are 9.4 and 9.6 eV, respectively. The value of 9.4 eV is to be compared with values in the range from 9.16 to 10.34 eV computed by Gutsev and the experimental value[1] of 9.60±0.05 eV which we have assigned to this transition. All these values are in reasonable agreement. The theoretical value of 9.62 eV for the transition from $SF_5^\bullet$ (C_{4v}) to SF_5^+ (C_{4v}) is lower than the (corrected) experimental values[1] which range from 10.4±0.3 eV to 11.0±0.3 eV. A preliminary search in our theoretical study for a transition state for the isomerization of SF_5^+ points toward a high barrier for this isomerization which is consistent with the observation of two states of this ion in the SIFT experiments.

We have chosen as the best available $\Delta H_f^0(SF_5^\bullet)$ the value of -218.7 ± 4.2 kcal mol^{-1} at 0 K reported recently by Fisher *et al.*[1] which becomes -221.1 ± 4.2 kcal mol^{-1} at 298 K, and we assign this value to the low energy C_{4v} isomer. IE($SF_5^\bullet$) = 9.60±0.05 eV[1] then provides standard enthalpies of formation for the low energy D_{3h} isomer of SF_5^+ of 2.7±5.4 and 0.3±5.4 kcal mol^{-1} at 0 and 298 K, respectively. The computed energy difference of 1.57 eV between the two isomers of $SF_5^\bullet$ yields $\Delta H_{298}^0(SF_5^\bullet, D_{3h}) = -184.9(\pm 4.2)$ kcal mol^{-1}. Taking a lower limit of 9.62 eV for the transition $SF_5^\bullet$ (C_{4v}) to SF_5^+ (C_{4v}) gives a lower limit for $\Delta H_{298}^0(SF_5^+, C_{4v}) = 0.7(\pm 4.2)$ kcal mol^{-1}.

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