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Article

Theoretical Study of the Gas-Phase Reaction: $SF_6 + CO^+ \Leftarrow SF_5^+ + FCO$

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Cálculos teóricos utilizando conjuntos de funções de base com potenciais efetivos de caroço (pseudopotencial ECP) foram efetuados para um grande número de sistemas moleculares relacionados a SF_6. Utilizou-se cálculos do tipo Hartree-Fock (HF), MP2 e QCISD(T). Foram feitos estudos para propriedades de estrutura eletrônica como geometrias moleculares, energias de dissociação de ligação e de ionização adiabática. No caso de estruturas moleculares, observou-se existir boa concordância entre os dados obtidos com pseudopotencial e aqueles disponíveis na literatura. Para propriedades relacionadas com energias, os métodos com pseudopotencial reproduzem a tendência observada usando cálculos mais sofisticados. O estudo da reação de SF6 com CO^+ foi caracterizado pela formação de um complexo íon-molécula reagente passando por um estado de transição e originando um complexo íon-molécula produto. Nesta reação, nem o estado de transição, nem o complexo íon-molécula reagente puderam ser localizados usando energias e forças do método HF, pois a reação prossegue sem barreiras formando SF_5^+ + FCO, sem uma barreira potencial associada ao processo. O uso de cálculos a partir de metodologia CASSCF(7,7)/B0 foi necessário para caracterizar o complexo íon-molécula reagente como ponto estacionário. Finalmente, estudos mais detalhados foram feitos para averiguar as mudanças na energia e na distribuição de cargas com o avanço da reação de reagentes para produtos. Observou-se que a reação $SF_6 + CO^+ \Leftarrow SF_5^+ + FCO$ ocorre via abstração de F^-, com a barreira de energia eletrônica de 103.86 kJ mol^{-1}.

Theoretical calculations using effective core potential (ECP) based methods were performed for a large number of molecular systems related to SF_6. Hartree-Fock (HF), MP2 and QCISD(T) methods were used. The quantities computed include equilibrium molecular geometries, bond dissociation energies, and adiabatic ionization energies. Where possible these quantities are compared with information available in the literature. The equilibrium geometries produced using the ECP-based methods are in very good agreement with structures reported in the literature. For the various energy differences, corresponding to the processes listed above, the ECP-based energies reproduce the trends. In addition to calculations on individual molecules, the reaction of SF_6 with CO^+ was studied. The first objective was to locate the reactant ion-molecule complex, the transition state, and the product ion-molecule complex for each of these systems. In this reaction neither a transition state nor a reactant ion-molecule complex could be located using HF-based forces and energies, reaction seemed to pass without a barrier to SF_5^+ + FCO. The use of a CASSCF(7,7)/B0 method was required to find the reactant ion-molecule complex. Finally more detailed studies were made of how the energy and charge distribution change as the reaction proceeds from reactants to products. It was observed that the reaction $SF_6 + CO^+ \Leftarrow SF_5^+ + FCO$ occurs *via* F^- abstraction, with the electronic energy barrier of 103.86 kJ mol^{-1}.

Keywords: gas phase reactions, anthropogenic chemical compound, QCISD(T), pseudopotential

Introduction

Gas phase reactions between molecules and ions, and molecules and electrons are known to be important in many scientifically and technologically important environments.[1-3] On the cosmic scale, the chemistry that produces molecules in interstellar clouds is dominated by ion-molecule reactions. Shrinking down to our own planet, the upper atmosphere is a plasma, and contains electrons and various positive ions. Certain anthropogenic chemical compounds[4]

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(including SF_6 and perfluorocarbons) can probably not be destroyed within the troposphere or stratosphere, but may be removed by reactions with ions or electrons in the ionosphere. SF_6 is a highly potent greenhouse gas used in the industry for insulation and current interruption in electric transmission and distribution equipment. It represents about 15% of total European fluorinated greenhouse gas emissions.[5]

Recent years have seen a massive growth in the industrial use of plasmas, particularly in the fabrication of microelectronic devices and components.[6] The chemistry within the plasma, much of which involves ion-molecule and electron-molecule reactions, determines the species that etch the surface, and hence the outcome and rate of an etching process. Much of the chemistry that is often labeled as ‘organic’ or ‘inorganic’ involves ion-molecule reactions, usually carried out in the presence of a solvent. For instance, S_{N2} reactions, such as $OH^- + CH_3Cl$, fall into this category. To gain a clearer picture of how these reactions occur, it is advantageous to study them removed from the (very great) perturbations due to the solvent. The experimental analysis is very difficult in many situations. So, the theoretical calculations can be useful. What can theoretical calculations add to the experimental data? It is possible to calculate the energies of each of the species involved in a specific reaction pathway, and so establish whether the reaction is exothermic. Theory is particularly powerful for providing energies of transient species such as ions, where experiments are usually only able to supply bounds. Inevitably there are questions about the accuracy of the energies provided by theoretical calculations, since all computational approaches contain approximations. Theory can be used to map out the detailed pathway that connects reactions to products.[7] For an ion-molecule reaction there may be three stationary points, a reactant ion-molecule complex, a transition state, and a product ion-molecule complex. For some exothermic reactions, there may be only one stationary point, a product ion-molecule complex. Examining the minimum energy pathway produced by theoretical calculations can then identify barriers and bottlenecks to reactions, and hence may reveal why some exothermic reactions have rate coefficients less than the predictions of capture theory.

The molecule SF_6 is widely used in plasmas for processing of materials, and the fabrication of microelectronic components.[6] Due to its very great technological importance there have been a number of studies of its reactions, and particularly those with ions and electrons, which are likely to be of importance in understanding the chemistry of SF_6 containing plasmas.[6,8-10,11-13] Richard D. Ernst and coworkers[14] have observed the high reactivity between SF_6 and low valent organometallic compounds of titanium and zirconium. They suggest that SF_6 may prove useful for preparing compounds “not normally obtained through other reactions.”

There has been much theoretical work on the energies of SF_n, SF_n^+, and SF_n^- molecules. The rate constants and product ion distributions have been measured for the reactions of many ions and also electrons with SF_6. Until this work there had been no attempt to use theoretical methods to map out the detailed pathway of any ion-molecule reaction of SF_6. On the basis of experimental evidence it has been asserted that the reaction of SF_6 with CO^+ proceeds via F^- abstraction.

Computational Methods

The scale of the problem must be reduced if any results are obtained. In order to obtain energies that may approach chemical accuracy (| |10 kJ mol^{-1}) calculations must take account of electron correlation. The ‘ideal’ methodology would have been a multi-reference configuration interaction all electron calculation with several large, flexible basis sets to enable extrapolation to the complete basis set limit. By the standards of high level ab initio quantum chemistry, the system SF_6 + CO^+ is large. So, performing accurate calculations (methodology and basis sets) on these systems represents a significant challenge. Morgon *et al.*[15-20] have been developing techniques to tackle such problems. These are centered around the use of effective core potentials (ECP),[21] in which the inner electrons are represented by an effective potential derived from calculations on atoms. The electronic wavefunction itself then only contains the outer electrons. Basis functions for these outer electrons are generated so that when used with the effective core potential important data are reproduced accurately. In fact two sets of basis functions were used, a small basis (usually called basis B0) and a larger basis, with extra diffuse and polarization functions (basis sets designated as B1). These diffuse functions are obtained by observing the convergent behavior of the weight functions (graphical display of the linear combination of basis functions[15,22]) of the outer atomic orbitals (s and p). Calculations with basis B1 are naturally much more expensive than those employing basis B0, so it is important to have computational schemes that perform the minimum number of calculations using basis B1.

Optimization of the molecular geometries and vibrational analysis are carried out at HF/B0 level. The harmonic frequencies confirm that the stationary points correspond to minima and are used to compute the zero-point energies. Further optimization is carried out at MP2/B0 level. At the MP2 equilibrium geometry corrections to the total energies are performed at higher level of theory. First, this is done to the QCISD(T)/B0 level, and later by addition of extra functions (s, p, d and f) at MP2/B1 level. Thus, these results coupled to additive approximations for the energy yield an effective calculation at a high level of theory,

$$E[QCISD(T)/(B1)] \mid E[QCISD(T)/(B0)] + \\ + E[MP2/(B1)] - E[MP2/(B0)] \qquad (1)$$

This scheme has been tested on a range of smaller systems, and shown to give good results.

All of these calculations were performed using the Gaussian98 program.[23] It should be noted that the absolute values of the calculated energies have no real significance, as no common energy zero for different atoms has been used. This arises from how the effective core potentials are constructed. When differences are formed, the differences between the zeros cancel, to leave for instance the difference in energy between the products and reactants of a reaction.

Results and Discussion

Initial Tests

There have been several attempts to produce a consistent set of energies for the SF_n, and SF_n^+ molecules. Of importance to this study are the G2 calculations of Irikura,[24] and the higher level calculations of Bauschlicher & Ricca (B&R).[25] G2 is a set of rules, containing empirical corrections, for obtaining energies which perform well in tests against experimental data. Bauschlicher & Ricca's work did not call upon empirical rules, but did look very carefully at the effect of basis set size. Their results appear to the best currently available in the literature. We used them to perform a series of tests on the energies produced by the ECP-based QCISD(T)/B1//MP2/B0 energies (equation 1). Specifically, comparisons were made between the structures of the SF_n and SF_n^+ molecules, S-F bond dissociation energies (BDE) and the adiabatic ionization energies (AIE) of SF_n molecules.

A comparison of molecular geometries, considering the ground states, for SF_6, SF_n, and SF_n^+ (n = 1 - 5) is presented in Table 1. The adiabatic ionization energies of the SF_n (n = 1 - 5) given by process $SF_n \Leftarrow SF_n^+ + e^-$, can also be obtained from the energies of the neutral SF_n molecules and the SF_n^+ cations, to provide another test of the quality of the energies produced from the QCISD(T)/B1//MP2/B0 calculations. The results can be found in Table 2. The first observation must be the excellent agreement between our values and those of Bauschlicher and Ricca (average error of 0.01 eV).

The results for the bond dissociation energies of the neutral SF_n molecules are tabulated in Table 3. These can be compared against dissociation energies from high level theoretical calculations (Bauschlicher and Ricca's results at RCCSD(T) level which have been extrapolated to the complete basis set limit) and also against a set of dissociation energies obtained from the G2 (results obtained from Irikura[24] and G3 calculations.

The general conclusions from these tables and graphs are that the ECP-based[21] calculations produce excellent optimized molecular geometries and the energy obtained using QCISD(T)/B1//MP2/B0 does a good job of reproducing the trends in the adiabatic ionization energies (AIE) and bond dissociation energies (BDE). The values of IE and BDE calculated in this work were compared with the medium values of previous results and are in the range of 0.05 to 0.49 eV (Table 2), and 0.97 to 7.70 kJ mol^{-1} (Table 3), respectively, and the calculations with this scheme are naturally much less expensive than procedures employing G2, G3, and complete basis sets.

The reaction between SF_6 and CO^+

The experimental observations concerning the reaction between SF_6 and CO^+ are that it is a fast reaction (k = 9.2×10^{-10} cm^3 molecule^{-1} s^{-1}), with an efficiency approaching 100%.[13] The only observed ion product is SF_5^+. Without identification of the neutral product(s) it is not possible to say for certain, on the basis of the experimental data, how the reaction proceeds.

It could be by dissociative charge transfer:

$$SF_6 + CO^+ \Leftarrow SF_5^+ + F + CO$$

or F^- abstraction:

$$SF_6 + CO^+ \Leftarrow SF_5^+ + FCO$$

On the basis of other evidence, and in particular that Kr^+,[13] which has a very similar recombination energy to CO^+, does not react with SF_6, it is strongly believed that the reaction proceeds by an F^- transfer mechanism. The experimental results[13] involving the CO^+ reagent ion and SF_5^+ product ion (100%) show that when the proposed neutral products are CO + F or FCO, the enthalpies ($\pm {}_{f}H_0^{O}$) have the values of +16 kJ mol^{-1} and -133 kJ mol^{-1}, respectively. This hypothesis can be tested through theoretical calculations. It is possible to map out the minimum energy pathway between the separated reactants and products. The high rate constant implies that there can be little or no activation energy barrier to the reaction. Characterization of the pathway requires the identification of three stationary points on the potential energy surface (together with the separated reactants and products). These are the reactant

Table 1. Molecular geometries and ground state symmetries for SF_6, SF_n, and SF_n^+ (n = 1 - 5) calculated at the MP2 level[a]. Where there are chemically distinct types of fluorine atom in a molecule, the subscript 1 refers to the less numerous or axial type. Distances are in Å and angles in degrees

Molecule	Point Group	Ground State	r_1	r_2	τ_{11}	τ_{12}	τ_{22}
SF	$C_{\Re v}$	^2I	1.627				
			(1.636)[b]				
SF_2	C_{2v}	$^1A_1$	1.620		99.2		
			(1.629)		(98.3)		
SF_3	C_s	$^2A'$	1.601	1.672	87.8	157.5	
			(1.600)	(1.700)	(88.1)	(160.1)	
SF_4	C_{2v}	$^1A_1$	1.663	1.585	171.1	87.2	102.0
			(1.688)	(1.585)	(172.5)	(87.6)	(100.7)
SF_5	C_{4v}	$^2A_1$	1.577	1.623	91.4	90.0	
			(1.576)	(1.630)	(91.5)	(90.0)	
SF_6	O_h	$^1A_{1g}$	1.593				
			(1.592)				
SF^+	$C_{\Re v}$	^3M	1.540				
			(1.536)				
SF_2^+	C_{2v}	$^2B_1$	1.540		101.9		
			(1.536)		(101.0)		
SF_3^+	C_{3v}	$^1A_1$	1.536		99.5		
			(1.531)		(99.1)		
SF_4^+	C_{2v}	$^2A_1$	1.575	1.526	160.3	96.0	104.1
			(1.574)	(1.525)	(161.1)	(95.8)	(104.0)
SF_5^+	D_{3h}	$^1A_1'$	1.558	1.533	180	90	120
			(1.552)	(1.524)	(180)	(90)	(120)

[a] Results at MP2=Full/6-31G* calculations.[24]; [b] Our results at the MP2/B0 level are in parentheses.

Table 2. Adiabatic Ionization Energies (in eV)

Molecule	Exp.[24]	B&R[25]	QCISD(T)/B1
S	10.36	10.34	9.86 (0.49) [a]
SF	10.16± 0.17	10.22	9.94 (0.25)
SF_2	10.08	10.15	10.07 (0.05)
SF_3	8.18 ± 0.07	8.24	8.60 (0.39)
SF_4	11.69 ± 0.06	11.90	11.98 (0.19)
SF_5	9.60 ± 0.05	9.52	10.02 (0.46)

[a] Values in parentheses are given by: $| x_{calc} - \frac{1}{2}\sum_{i=1}^{2} x_i |$ where x_i is the experimental measurement or previous theoretical result.

ion-molecule complex, the transition state, and the product ion-molecule complex.

Initial HF/B0 searches starting from a variety of start geometries failed to find either a reactant ion-molecule complex or a transition state. Each run either aborted for one reason or another, or optimized to a product ion- molecule complex comprising SF_5^+ and FCO. No runs terminated with a complex made up of SF_5^+ + F + CO. The reaction clearly proceeds by a F^- transfer mechanism, but the transition state had not been found. The system SF_6/CO^+ is difficult because of the high symmetry of the molecules, and the open shell electronic structure. This implies that there are likely to be several molecular orbitals for the system with energies close to (but above) the highest occupied molecular orbital. A single determinant electronic wavefunction of the type used in Hartree-Fock calculations is then a poor description of the system. A better starting wavefunction was obtained using the CASSCF(7,7)/B0 (Complete

Table 3. Total Electronic Energies (in a.u.), Zero-point Vibrational Energies (in a.u.), and Bond Dissociation Energies, $SF_n \Leftarrow SF_{n-1} + F$ (at 298.15K)

System [a]	E[MP2/B0]	E[QCISD(T)/B0]	E[MP2/B1]	ZPE[HF/B0] [b]
F (^2P)	-24.028646	-24.042005	-24.051544	-
S (^3P)	-9.999575	-10.020216	-10.032077	-
SF ($C_{\Re v}$, ^2I)	-34.137353	-34.164851	-34.221445	0.0018
SF_2 (C_{2v}, $^1A_1$)	-58.291107	-58.322276	-58.426410	0.0045
SF_3 (C_s, $^2A'$)	-82.394242	-82.429456	-82.575967	0.0069
SF_4 (C_{2v}, $^1A_1$)	-106.556833	-106.593556	-106.792040	0.0115
SF_5 (C_{4v}, $^2A_1$)	-130.636391	-130.676614	-130.915668	0.0155
SF_6 (O_h, $^1A_{1g}$)	-154.817522	-154.859572	-155.146651	0.0213
		BDE (kJ mol^{-1})		
	G2 [d]	G3	B&R [e]	QCISD(T)/B1
SF	349.1	347.41	350.03	343.55 (5.30) [c]
SF_2	378.0	370.05	377.56	374.23 (0.97)
SF_3	230.8	227.17	225.85	229.76 (1.82)
SF_4	403.4	395.46	406.18	393.98 (7.70)
SF_5	163.8	163.26	157.57	157.62 (3.92)
SF_6	449.9	442.14	453.25	431.46 (16.97) (5.89) [f]

[a] The effects of spin-orbit coupling on the energies have been neglected. [b] The HF/B0 vibrational wavenumbers are scaled by the standard factor 0.8929.
[c] Values in parentheses are given by: $|x_{calc} - \frac{1}{3}\sum_{i=1}^{3} x_i|$ where x_i is the value of the previous theoretical result. [c] [d] G2 calculations of Irikura.[24]
[e] Accurate Heats of Formation for SF_n (n = 1 - 6), obtained by Bauschlicher & Ricca.[25] [f] $D^o_{298}(SF_5\text{-}F) = 420 \pm 10$ kJ mol^{-1}.[29]

Active Space Self Consistent Field) method. It was then possible to locate the reactant ion-molecule complex. This geometry was then used in the subsequent HF/B0 calculations of frequencies, and MP2/B0, QCISD(T)/B0, and MP2/B1 calculations of the energy of the reactant ion-molecule complex. The electronic energies for systems in SF_6/CO^+ reaction are summarized in Table 4.

The relative energies of the separated reactants, the reactant ion-molecule complex, the transition state, the product ion-molecule complex, and the separated products Xat the QCISD(T)/B1//MP2/B0 level – equation 1, are displayed in Figure 1. There are no strong forces in the product ion-molecule complex, and minimum energy structures corresponding to a variety of different structures were found by HF/B0 followed by MP2/B0 optimizations. The transition state lies far in energy below the separated reactants, it is unlikely to act as a significant bottleneck to the reaction, which is consistent with the experimental observation that the reaction is not less than 70% efficient.[13]

This transition state (TS) ($\rho_i = 478.80$ cm^{-1}) shows a close approach of the CO^+ to the SF_6, and that when first formed the SF_5^+ unit has approximately C_{4V} symmetry (for the isolated SF_5^+ molecule the equilibrium geometry has D_{3h} symmetry). The Figure 2 shows the intrinsic reaction coordinate (IRC) pathway. The IRC was calculated using HF/B0 theory. The reaction path is formed through the computation of an IRC

Table 4. Total electronic energies and (in .a.u.) and zero-point vibrational energies (ZPEs in a.u.) for systems in SF_6/CO^+ reaction

System	E[MP2/B0]	E[QCISD(T)/B0]	E[MP2/B1]	ZPE[HF/B0] [a]
CO^+	-21.015803	-21.048628	-21.047928	0.0046
FCO	-45.617317	-45.644679	-45.683091	0.0080
SF_5^+	-130.271288	-130.309434	-130.487573	0.0177
SF_6	-154.817522	-154.859572	-155.073521	0.0212
$[SF_5 \cdot FCO]^+$	-175.892968	-175.959415	-176.177401	0.0263
$[SF_5 \cdot F \cdot CO]^{+(\#)}$	-175.860251	-175.933023	-176.146680	0.0251
$[SF_6 \cdot CO]^+$	-175.845220	-175.923740	-176.147297	0.0260

[a] The ZPE[HF/B0] are scaled by the standard factor 0.8929.

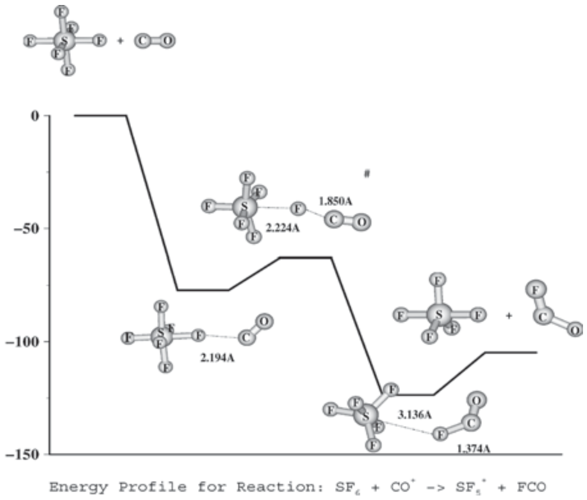

Figure 1. Energy profile for reaction: SF$_6$ + CO$^+$ $\Leftarrow$ SF$_5^+$ + FCO

using the Gonzalez-Schlegel second order method[26] to connect the reactant to the transition state and then to the product. The IRC is interpreted as the pathway of a concerted mechanism involving a single TS. To investigate the reaction pathway further (Figure 1), the HF/B0 energy and the charge distribution (as expressed by the Mulliken atomic charges) were calculated as the F$^-$ was abstracted from the SF$_6$. At each separation of the F from the S the energy was optimized (subject to the constraint that the SF$_5$ unit retained C$_{4v}$ symmetry), and the Mulliken atomic charge were calculated, subsequently the atomic charges were summed to give the charges on the SF$_5$, F and CO units (Figure 3). Due to the time required to perform the many geometry optimizations the calculations were limited to the HF/B0 level. Inspection of the energy plot shows a smooth variation (there is no maximum corresponding to a transition state in HF/B0 calculations on this system). The charges also vary smoothly as the S-F distance extends. This smooth variation of the charges and energies is expected for a reaction occurring on the potential energy surface for a single electronic state of the overall system. This is further proof that the SF$_6$ + CO$^+$ reaction occurs via a F$^-$ transfer mechanism (with the value of 103.86 kJ mol^{-1}).

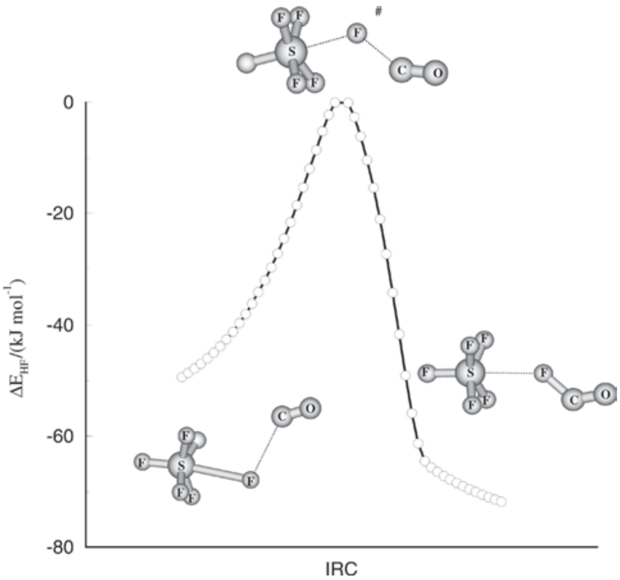

Figure 2. Intrinsic Reaction Coordinate

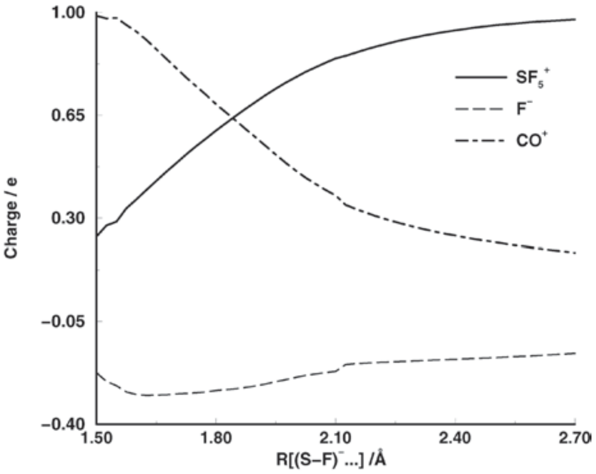

Figure 3. Mulliken charges versus R [(S-F)$^-$ • • •] in [SF$_6$ • • • CO]$^+$ (SF$_5^+$ constrained to C$_{4v}$)

Additional information can be given by the kinetic constant calculation for the SF$_6$ + CO$^+$ $\Leftarrow$ SF$_5^+$ + FCO reaction. The reaction rate constant (k) was determined using the Conventional Transition-State Theory (CTST).[27,28] Considering a unimolecular process the CTST formula can be applied to calculate k:

$$k = \kappa \frac{k_B T}{h} \frac{Q_{SF_5.F.CO^{+\#}}}{Q_{SF_5.FCO^+}} e^{-\frac{E_a}{RT}} \tag{2}$$

where ξ is the tunneling factor, k_B and h are the Boltzmann and Planck constants, respectively. $Q_{SF_5.FCO^+}$ and $Q_{SF_5.F.CO^{+\#}}$ represent the partition functions corresponding to the reactant complex and transition state, and were obtained from the Gaussian98 output. E_a involves the difference between the high-level energies (QCISD(T)/B1) of reactant complex and TS, including ZPE corrections. The effect is essential in cases where high barriers and large frequencies occur, and this is not the case in the present reaction, so the ξ = 1 was considered. The value of k calculated at 298 K is approximately equal to 3.9×10^{-11} cm^3 molecule^{-1} s^{-1}, and this value is close to the experimental value,[13] $k_{\text{exp}} = 9.2 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} at 300 K.

Conclusions

ECP-based methods have been shown to be powerful, and of affordable computational cost for the systems addressed in this work. An exploration of the potential energy surface - at high level of theory including electron correlation - QCISD(T), for the F^- abstraction reaction of SF_6 with CO^+, including an examination of the charge distribution as the reaction (to $SF_5^+ + FCO$) proceeds. The reaction $SF_6 + CO^+ \Leftarrow SF_5^+ + FCO$ occurs via F^- abstraction and it is a fast reaction.

Acknowledgments

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Supplementary Information

Supplementary data are avaiable free of charge at http://jbcs.sbq.org.br. There are two sets of basis functions: *i)* a small basis (usually called B0) and *ii)* a larger one, with extra diffuse and polarization functions (designated as B1). The effective core potential (ECP) used is SBKJC potential for all atoms.

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Supplementary Information

Theoretical Study of the Gas-Phase Reaction: $SF_6 + CO^+ \Leftarrow SF_5^+ + FCO$

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Two sets of basis functions were used in this work, a small basis (B0) and a larger one, with extra diffuse and polarization functions (B1). The effective core potential (ECP) used was SBKJC potential[21] for all atoms.

Table S1. Small Basis Set (B0)

Atom	Function	Exponent	Coefficient
CARBON	S	0.038875	1.000000
	S	0.112798	1.000000
	S	0.327290	1.000000
	S	1.116069	-0.093440
		3.931696	-0.134350
		13.850610	-0.004060
		48.793033	-0.001890
	P	0.128347	1.000000
	P	0.420634	1.000000
	P	1.364696	0.214740
		4.490295	0.055280
		14.774539	0.012870
	D	0.511867	1.000000
OXYGEN	S	0.179148	1.000000
	S	0.481294	1.000000
	S	1.293032	1.000000
	S	3.414395	-0.080010
		8.879166	-0.116351
		23.090350	0.004502
		60.046660	-0.004333
	P	0.198142	1.000000
	P	0.693275	1.000000
	P	2.329895	0.327622
		7.995507	0.091601
		27.438202	0.018310
	D	1.160205	1.000000
FLUORINE	S	0.274726	1.000000
	S	0.884323	1.000000
	S	2.846573	1.000000
	S	9.542028	-0.132409
		30.811976	-0.007367
		99.494352	-0.001405
		321.275271	-0.000427
	P	0.268811	1.000000
	P	0.936091	1.000000
	P	3.134847	0.298814
		10.733386	0.083031
		36.749988	0.016849
	D	1.403647	1.000000
SULFUR	S	0.180126	1.000000
	S	0.555085	1.000000
	S	1.710576	1.000000
	S	5.298288	-0.018630
		16.502688	0.007291
		51.401259	0.000940
		160.100548	0.000032
	P	0.084825	1.000000
	P	0.235876	1.000000
	P	0.650758	0.382423
		1.911477	-0.041052
		5.614597	-0.014522
	D	0.526495	1.000000

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Table S2. Larger Basis Set (B1): Small Basis Set plus extra diffuse and polarization functions

Atom	Function	Exponent	Coefficient
CARBON	S	0.013397	1.000000
	P	0.039162	1.000000
	D	0.128347	1.000000
	F	0.128347	1.000000
OXYGEN	S	0.066683	1.000000
	P	0.056630	1.000000
	D	0.693275	1.000000
	F	0.693275	1.000000
FLUORINE	S	0.085347	1.000000
	P	0.077193	1.000000
	D	0.936091	1.000000
	F	0.936091	1.000000
SULFUR	S	0.058452	1.000000
	P	0.305047	1.000000
	D	0.235876	1.000000
	F	0.235876	1.000000