Ab Initio Calculations of Low-lying States of SF⁻

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Anion SF⁻ makes nonnegligible contribution to charged species composition of SF_6 decomposition products in low-temperature region. As no experimental data concerning excited states of the SF⁻ are available, ab initio calculations of the low-lying electronic states were performed using sophisticated multireference configuration interaction (MRCI) method to provide reliable estimates of the missing values for modelling the processes in which SF⁻ takes part. The potential curves of X $^1\Sigma^+$ and lowest singlet states $^1\Sigma^+$, $^1\Pi$, and $^1\Delta$ were calculated for interatomic distances ranging from 1.3 Å to 4 Å. The calculated X $^1\Sigma^+$ and 1 $^1\Pi$ states have minima at 1.726 Å and 2.092 Å respectively, whereas the remaining 1 $^1\Sigma^+$ and $^1\Delta$ states are repulsive. The obtained bond length of the ground state closely fits the experimental value of 1.717 Å. The MRCI results are justified to be used in further thermodynamic and/or kinetic calculations.

1. Introduction

The electrical conductivity of HV-EHV circuit breakers containing SF_6 depends primarily on the concentration of free electrons because of their high mobility along the direction of electric field, and, indeed, any change in concentration of free electrons substantially affects the conductivity and dielectric strength of the quenching medium [1]. The concentration of electrons, however, depends upon the concentration of other components, hence a proper determination of the composition of the system is necessary. When some neutral components begin to ionize, the produced electrons can both recombine with cations and attach the neutrals to form negative ions. If the system contains substances possessing electron affinity of sufficiently high magnitude, then the concentration of free electrons might substantially decrease. Numerical studies of the reaction kinetics of quenching process in circuit breakers with SF_6 after current zero show non-negligible fraction of SF⁻ in kinetic composition, and indicate that, as the composition approaches the equilibrium, the concentration of SF⁻ predominates over that of other anions and electrons [2,3]. The anion SF⁻ plays important role in such processes of electron transfer and its presence should not be omitted if SF_6 containing plasma is to be treated by a numerical model. The first step in modelling the plasma processes is represented by the calculation of the composition and thermodynamic functions describing a gaseous system in thermodynamic equilibrium [4]. Such a calculation is based on the knowledge of standard thermodynamic functions of individual molecules, which implies the need for the quantum mechanical description of the molecular

states. Furthermore, there is a growing interest in the calculating of transport properties by means of evaluation of collision integrals on the basis of molecular interaction potentials [5,6]. As to SF⁻ anion, the data concerning the microscopic description of the molecular states are far from being complete. Some experimental data concerning ground state geometry are reported in [7], and *ab initio* coupled-cluster calculations of spectroscopic constants are in [8], however, neither theoretical calculations nor experimental results have been published for excited states. In this work, the multireference configuration interaction method (MRCI) was used to produce reliable interatomic potentials for some low-lying excited electronic states of negatively charged SF⁻ molecules. Nowadays, MRCI method [9] is well established and capable of predicting both excitation energies and molecular geometries [10] by multireference approach.

2. Methods and Computational Details

The initial reference state vectors were determined at the complete active space self-consistent field (CASSCF) level of theory, where state-averaged natural orbitals were taken as the starting orbitals for subsequent MRCI calculations. A full valence set of orbitals was generated to form complete active space configurations, and as the N-electron basis for the CI problem Slater determinants were chosen. All the CASSCF calculations were performed by quadratically convergent method of Knowles and Werner [11,12]. Note that convergence of optimized states to the correct symmetry corresponding to Λ within linear $C_{\infty v}$ point group was forced by a transformation of Hamiltonian of primary space into

symmetry adapted basis (eigenvectors of Λ^2). The reference configurations for the subsequent CI stage of calculation were then selected from the state averaged CASSCF state vectors generated for the desired symmetry. Multireference configuration interaction including single and double excitation (MRCISD) for all states of given symmetry was performed using internally contracted CI algorithm of Knowles and Werner [13,14]. The convergence threshold for energy was 10^{-8} Hartree and the threshold for CI-vector, defined as the square of sum of the changes in CI-coefficients was 10^{-6}. These thresholds were kept the same in all the calculations. The reference space was spanned by 8 configuration state functions (CSF) in C_{2v} symmetry, which corresponds to 8 active orbitals consisting of four σ orbitals and two π ones. Core orbitals were selected from atomic inner shells as $(1\text{-}4\sigma)$, (1π). There were 155 external orbitals and 14 electrons in valence space. Some other choices of the parameters entering into MRCI calculations are shown in Table 1.

Table 1 Summary of technical details. For each symmetry species, the number of state averaged CASSCF states forming the starting vectors for CI (SA-CAS), number of optimized CI roots (NROOT) and the number of reference states (REF) are listed.

Species	SA-CAS	NROOT	REF
Σ^+	3	3	3
Π	8	1	8
Δ	4	1	1

The basis set used in all calculations consists of well known correlation consistent basis sets [6s, 5p, 4d, 2f, 1g] (cc-pV(Q+d)Z, see [15]) centered at S and the basis set [5s, 4p, 3d, 2f, 1g] (cc-pVQZ, see [16]) centered at F. Atoms S and F were augmented by diffuse functions (1s, 1p, 1d, 1f, 1g) (reference [15] and [17] respectively). These basis sets were obtained from EMSL Basis Set Library [18]. To describe the proper shape of potential functions, the total energy was computed in multiple points, starting from 1.3 Å to 5.5 Å. All the computations were performed by using MOLPRO quantum chemistry package [19]. The resulting MRCISD energies were also automatically corrected to estimate full CI limit by virtue of Davidson formula. To find the equilibrium bond distance, r_e, for the bound states, the final values of total energies were fitted to a polynomial expansion, in terms of $(r-r_e)/r_e$, of degree 8.

3. Results and Discussion

The resultant MRCI interatomic potentials for internuclear distances ranging from 1.3 Å to 4 Å are depicted on Fig. 1. The optimized equilibrium geometries and corresponding adiabatic excitation energies are summarized in Table 2.
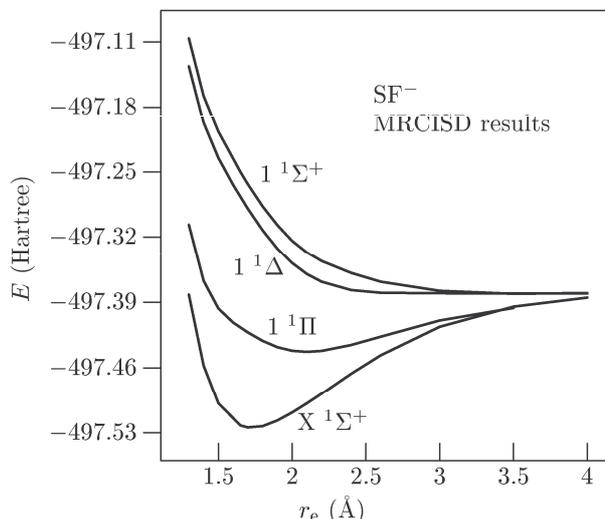

Fig. 1 The MRCISD calculated interatomic potential curves corrected to full CI estimates.

All the states (see Fig. 1) tend to the same dissociation limit $^3P_g(S) + {}^3P_g(F^-)$.

In the case of $^1\Sigma^+$ states, the first excited $1\ ^1\Sigma^+$ is clearly a repulsive one. In contrast to the smaller internuclear distances up to 4 Å, the correlation energy is at distances exceeding 4 Å (data not shown) strongly influenced by considerably increased fraction of double excitations from π orbitals of reference configurations, which leads to lowering the magnitude of correlation energies for the two successive distances of 4 Å and 4.5 Å to about 1.8 eV (the corresponding energies at CASSMP2 level of theory [20] show no such the growth beyond 4 Å).

Table 2 Electronic states, dominant configurations in vicinity of equilibrium geometry (if any) and adiabatic excitation energies T_e in eV together with equilibrium interatomic distances r_e in Å. Core stands for $(1\text{-}4\sigma)^2 (1\pi)^4$.

State	Configuration	T_e	r_e
X $^1\Sigma^+$	Core $(5\text{-}7\sigma)^2 (2\text{-}3\pi)^4$	0.0	1.726
$1\ ^1\Sigma^+$	Core $(5\text{-}8\sigma)^2 (2\pi)^4 (3\pi)^2$		
$1\ ^1\Pi$	Core $(5\text{-}7\sigma)^2 (8\sigma)^1 (2\pi)^4 (3\pi)^3$	2.2	2.092
$1\ ^1\Delta$	Core $(5\text{-}8\sigma)^2 (2\pi)^4 (3\pi)^2$		

The obtained bond length for the ground state, 1.726 Å, is somewhat larger than the reported experimental value 1.717 Å [7], the corresponding

CCSD(T) value being 1.724 Å [8] and the dissociation energy is approximately 3.9 eV. The 1 $^1\Pi$ state is the bound one, nevertheless the minimum is a rather shallow, with energy of dissociation about 1.7 eV, and when approaching larger distances, the strongly multiconfigurational character is detected. The last calculated state 1 $^1\Delta$ exhibits a repulsive behaviour.

4. Conclusions

In this work, adiabatic potential curves for the lowest singlet states of Σ^+, Π, and Δ spatial symmetry state of SF^- anion were determined by MRCI method. Since this method is based on the multireference approach, it is justified to regard the obtained potential curves as proper estimates of missing experimental values. This potential may thus be used in further calculations of collision integrals, and/or partition function. Extension of the present investigations to higher states including triplet multiplicity is in progress. The unreported results are available upon request.

Acknowledgement

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[19] MOLPRO version 2006.1. MOLPRO is a package of ab initio programs written by H.-J. Werner, P. J. Knowles, R. Lindh, F. R. Manby, M. Schütz, P. Celani, T. Korona, G. Rauhut, R. D. Amos, A. Bernhardsson, A. Berning, D. L. Cooper, M. J. O. Deegan, A. J. Dobbyn, F. Eckert, C. Hampel, G. Hetzer, A. W. Lloyd, S. J. McNicholas, W. Meyer, M. E. Mura, A. Nicklaß, P. Palmieri, R. Pitzer, U. Schumann, H. Stoll, A. J. Stone, R. Tarroni, and T. Thorsteinsson.

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