Binary molecular complexes of silicon tetrafluoride with water, methanol, and dimethyl ether. Quantum-chemical study

S. K. Ignatov,a* P. G. Sennikov,b A. G. Razuvaev,a and L. A. Chuprovab

aN. I. Lobachevsky University of Nizhniy Novgorod, 23 prospekt Gagarina, 603600 Nizhniy Novgorod, Russian Federation. Fax: +7 (831 2) 65 8592. E-mail: ignatov@ihchem.unn.runnet.ru
bInstitute of High-Purity Substances, Russian Academy of Sciences, 49 ul. Tropinin, 603600 Nizhniy Novgorod, Russian Federation. Fax: +7 (831 2) 66 8666. E-mail: sen@ihps.novnu.ru

The molecular structures, the energies of complex formation, and the vibrational spectra of the binary molecular complexes of SiF4 with water, methanol, and dimethyl ether were calculated by the ab initio MP2 method with the basis sets up to 6-311++G(2d,2p). In the complexes, which have been detected previously by IR spectroscopy in low-temperature (12–15 K) inert matrices, the five-coordinate Si atom is in a distorted trigonal-bipyramidal environment, which is formed through the donor-acceptor interaction of the O atom with the Si atom and is additionally stabilized by the H...F hydrogen bonds.

Key words: silicon tetrafluoride, binary complexes, matrix isolation, ab initio quantum-chemical calculations.

Complexes of silicon halides with various ligands have been under investigation over many years.1–4 Most of studies were devoted to stable compounds, which were isolated in the individual form and bore, primarily, nitrogen-containing ligands.5–7 whereas complexes with oxygen-containing ligands have been less studied. In the early studies,8–10 the solid 1 : 4 and 1 : 2 adducts of SiF4 with MeOH and ethers were isolated. These adducts were prepared by the reactions of SiF4 with methanol and ethers at room or lower temperatures. The molecular structures, the nature of the chemical bonds, and the vibrational spectra of these compounds are still open questions.11 The formation of weak gas-phase complexes with oxygen-containing donors, including water and low-molecular-weight organic molecules, are much less studied.12 However, this information is gaining in importance because of a wide use of highly pure SiF4 in new fields of technology. When analyzing the efficiency of different procedures for the purification of SiF4, one should take into account the possibility of chemical reactions of the main compound with H2O impurities as well as of solvolysis and exchange reactions with organic compounds. Generally, these reactions proceed at low temperatures whereby binary complexes, which are unstable under ambient conditions, are put in the forefront.

The binary complexes of SiF4 with water, methanol, and dimethyl ether were first experimentally discovered by IR spectroscopy in low-temperature (12–15 K) argon and nitrogen matrices. These complexes were described as compounds of compositions SiF4·H2O, SiF4·MeOH, and SiF4·Me2O in which the chemical bond is formed through the partial electron density transfer from the molecule of the oxygen-containing compound to the SiF4 molecule.12 The ab initio MP2/6-311++G(d,p) calculations of the fragments of the potential energy surface (PES) for the SiF4·H2O system revealed the only stable complex of composition SiF4·H2O, which contains the five-coordinate Si atom and the donor-acceptor Si...O bond formed through the partial electron density transfer from the O atom of the H2O molecule to the σ-orbitals of the Si atom. The calculated frequency shifts in the IR spectra that occur upon the formation of this complex agree well with the experimental values obtained in a low-temperature matrix. Under the conditions of an inert matrix, the formation of the octahedral SiF4·2H2O complexes is energetically unfavorable and no local minima on the potential energy surface correspond to hydrogen-bonded structures. Nevertheless, the molecular structure, the energy, and the spectral characteristics of the complexes of SiF4 with low-molecular-weight oxygen-containing organic ligands remained unknown. In addition, there is no direct evidence that the complexes of SiF4 with organic ligands found previously are binary donor-acceptor compounds structurally related to SiF4·H2O.

In the present study, we undertook a theoretical investigation of the molecular structures, the energies of complex formation, and the vibrational spectra of the complexes of SiF4 with H2O, MeOH, and Me2O for the purpose of making the assignments in the experimental IR spectra measured in a low-temperature solid matrix. Although the complexes of SiF4 with water have been studied previously, we carried out calculations for this
system using a more complete basis set with the aim of refining the results and performing the correct comparison of the calculated values with those obtained for the SiF₄–MeOH and SiF₄–Me₂O systems. In addition, we carried out conformational analysis of the SiF₄·H₂O complex to estimate the effect of the internal rotation of the H₂O molecule on the structure of the complex, its energy, and vibrational frequencies.

**Calculation procedure**

All calculations were carried out by the *ab initio* SCF method with inclusion of the electron correlation according to the second-order Möller–Plesset perturbation theory (MP2) with the 6-311G++G(d,p), 6-311++G(2d,p), and 6-311++G(2d,2p) basis sets. In addition to the full geometry optimization, we calculated the vibrational frequencies and absolute intensities for all stationary points. All calculations were performed using the PC GAMESS program. Thermodynamic calculations were carried out with the use of the PC GAMESS program and the original MOLTRAN program, which takes into account the contributions of internal rotations of unhindered groups to thermodynamic functions. The correction for the basis set superposition error was made using the standard counterpoise method. The fragments of intermolecular PES for the SiF₄–H₂O and SiF₄–MeOH systems were examined using the original ADANIME program, which has specially been developed for rapid scanning of PES. In the studies of the internal rotation profiles, the energies at PES points were calculated with the use of the GAUSSIAN-94 program according to the MP2/6-311++G(d,p) and B3LYP/6-311++G(d,p) methods employing spherical (3d) polarization basis functions. Although the exponents of the polarization functions of the Si atom involved in the GAUSSIAN-94 program differ slightly from those employed in the GAMESS program, these differences (as well as the differences between the Cartesian and spherical functions) have no noticeable effect on the geometry of the structures under study and their relative energies.

**Results and Discussion**

The molecular structure of the SiF₄·H₂O complex was optimized at the MP2/6-311++G(d,p),

**Table 1. Bond lengths and bond angles in the starting compounds and the complexes optimized by the MP2 method with the use of different basis sets**

<table>
<thead>
<tr>
<th>Geometric parameter</th>
<th>Value</th>
<th>Geometric parameter</th>
<th>Value</th>
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<tr>
<td></td>
<td>SiF₄</td>
<td>SiF₄·MeOH</td>
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<td>Bond/Å</td>
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<td>Si...O</td>
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<td>O—H</td>
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<td>Angle/deg</td>
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<td>Si—F(2)</td>
<td>1.595</td>
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<td></td>
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<td>Si—F(3), F(4)</td>
<td>1.590, 1.593</td>
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*a* The calculations were carried out at the MP2/6-311++G(d,p) (I), MP2/6-311++G(2d,p) (II), and MP2/6-311++G(2d,2p) (III) levels. The atomic numbering scheme corresponds to that presented in Fig. 1.

*b* Data for the eclipsed and staggered conformations are given in the numerator and denominator, respectively.

*c* The distance between the H atom of the OH group and the nearest F atom.