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Structures, vibrational frequencies, and electron affinities of $SF_5O_n/SF_5O_n^-$ ($n = 1–3$)

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ABSTRACT

The molecular structures, vibrational frequencies, and electron affinities of the $SF_5O_n/SF_5O_n^-$ ($n = 1–3$) species have been examined with four hybrid density functional theory (DFT) methods. The basis set used in this work is of double-ζ plus polarization quality with additional diffuse s- and p-type functions, denoted DZP++. The geometries are fully optimized with each DFT method independently. The SF_5O_n ($n = 1–3$) species should be potential greenhouse gases. The anion $SF_5O_2^-$ with C_s symmetry has a $^3A''$ electronic state, and the neutral SF_5O_3 with $^2A''$ electronic state has C_s symmetry. The anions $SF_5O_2^-$ and $SF_5O_3^-$ should be regarded as $SF_5^-\cdot O_2$ and $SF_5O^-\cdot O_2$ complexes, respectively. Three different types of the neutral–anion energy separation presented in this work are the adiabatic electron affinity (EA_{ad}), the vertical electron affinity (EA_{vert}), and the vertical detachment energy (VDE). The EA_{ad} values predicted by the B3PW91 method are 5.22 (SF_5O), 4.38 (SF_5O_2), and 3.61 eV (SF_5O_3). Compared with the experimental vibrational frequencies, the BHLYP method overestimates the frequencies, and the other three methods underestimate the frequencies. The bond dissociation energies D_e ($SF_5O_n \rightarrow SF_5O_{n-m} + O_m$) for the neutrals SF_5O_n and D_e ($SF_5O_n^- \rightarrow SF_5O_{n-m}^- + O_m$ and $SF_5O_n^- \rightarrow SF_5O_{n-m} + O_m^-$) for the anions $SF_5O_n^-$ are reported.

1. Introduction

Recently, sulfur hexafluoride (SF_6) and its substituted radical SF_5CF_3 have been the subjects of numerous theoretical [1–4] and experimental [5–7] studies because of their effects on the environment. In addition, scientists have also proposed the use of molecules such as SF_6, SF_5CF_3, fluoroalkanes, and so on to terraform Mars [8]. In this study, we report the systematic investigation of $SF_5O_n/SF_5O_n^-$ ($n = 1–3$) species, which are products in photo-dissociation reactions of SF_6 and SF_5CF_3.

There are a few previous studies on these species both experimentally [9–10] and theoretically [11–13]. As early as 1973, Christe et al. [9] reported the experimental vibrational frequencies and assignment for SF_5O^-. In 2002, Arnold et al. [11] predicted a very high electron affinity for SF_5O, 5.14 eV. Not surprisingly, the anion SF_5O^- has been observed as a long-lived species in SF_6/H_2O plasmas [12]. The possible reaction mechanisms of SF_5O_2 have been presented by Sehested et al. [13] Some fundamental vibrational frequencies for the SF_5O_n series have been determined from infrared (IR) spectra with the matrix isolation technique [10]. But, at present, no electron affinities for SF_5O_2 and SF_5O_3 are known. Compared to the neutral SF_5O_n radicals, geometry parameters and chemical properties of the anions $SF_5O_n^-$ are scarce.

Density functional theory (DFT) in conjunction with DZP++ basis sets has been shown to be successful in predicting the electron affinity of many inorganic species, such as ClO_n/ClO_n^-, CF_3O/CF_3O^-, TiO_n/TiO_n^-, and BrO_n/BrO_n^- [14–18]. These studies and others have demonstrated that the hybrid DFT/DZP++ methods are able to accurately predict electron affinity. In addition, these methods are reliable to predict the geometry parameters for the neutral radicals and their anions.

The purpose of our work is to apply four modern DFT methods to predict the electron affinities of SF_5O_n ($n = 1–3$), as well as their equilibrium geometries, harmonic vibrational frequencies, and bond dissociation energies. Three forms of the electron affinity are reported, evaluated as the neutral–anion energy separation in the following manners.

The adiabatic electron affinity (EA_{ad}) is determined by, $EA_{ad} = E$ (optimized neutral) – E (optimized anion), the vertical electron affinity (EA_{vert}) by, $EA_{vert} = E$ (optimized neutral) – E (anion at optimized neutral geometry), and the vertical detachment energy (VDE) of the anion by, VDE = E (neutral at optimized anion geometry) – E (optimized anion).

2. Theoretical methods

The four hybrid Hartree–Fock/density functionals used in this work are: (a) Becke's three parameter hybrid exchange functional [19] with LYP correlation functional [20] (B3LYP); (b) Becke's three parameters hybrid exchange functional with the correlation

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functional of Perdew and Wang [21] (B3PW91); (c) Becke's three parameter hybrid exchange functional with Perdew's correlation functional [22] (B3P86); (d) the half and half exchange functional [23] with LYP correlation functional (BHLYP).

Unrestricted methods were used for all the opened-shell species, and restricted methods for the closed-shell species. All of the molecular structures and the electron affinities have been determined using the Gaussian 03 program suite [24]. The standard double-ζ plus polarization (DZP) basis set with the addition of diffuse functions was utilized. The DZ part of the basis set was constructed from the Huzinaga–Dunning–Hay [25–28] set of contracted double-ζ Gaussian functions. The DZP basis was formed by the addition of a set of five d-type polarization functions for each O, F, and S atom [α_d (F) = 1.00, α_d (O) = 0.85, α_d (S) = 0.70]. The DZP basis set was augmented with diffuse functions: O, F, and S received one additional s-type and one additional set of p-type functions. The diffuse function orbital exponents were determined in an "even-tempered sense" as a mathematical extension of the primitive set, according to the formula of Lee and Schaefer [29] [α_s (F) = 0.1049, α_P (F) = 0.0826, α_s (O) = 0.08227, α_P (O) = 0.06508, α_s (S) = 0.04267, α_P (S) = 0.04096]. The final basis set was thus F and O (10s6p1d/5s3p1d), and S (13s9p1d/7s5p1d). This extended basis set will be denoted as "DZP++".

All stationary point geometries were characterized by the evaluation of their harmonic vibrational frequencies at the four different levels of theory.

Besides the electron affinities, the bond dissociation energies for $SF_5O_n/SF_5O_n^-$ (n = 1–3) are also determined as the difference in total energies in the following manners.

The bond dissociation energies for the neutrals refer to the reactions:

$$SF_5O_n \rightarrow SF_5O_{n-1} + O,\ SF_5O_n \rightarrow SF_5O_{n-2} + O_2,$$
$$SF_5O_n \rightarrow SF_5O_{n-3} + O_3.$$

And the bond dissociation energies for the anions refer to the reactions:

$$SF_5O_n^- \rightarrow SF_5O_{n-1}^- + O,\ SF_5O_n^- \rightarrow SF_5O_{n-2}^- + O_2,$$

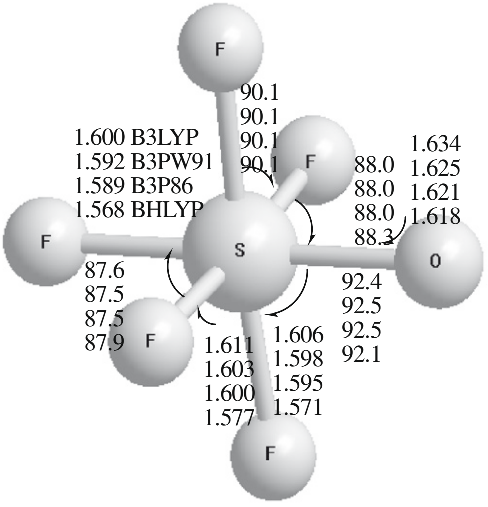
$$SF_5O_n^- \rightarrow SF_5O_{n-3}^- + O_3,\ \ SF_5O_n^- \rightarrow SF_5O_{n-1} + O^-,$$

$$SF_5O_n^- \rightarrow SF_5O_{n-2} + O_2^-,\ \ SF_5O_n^- \rightarrow SF_5O_{n-3} + O_3^-.$$

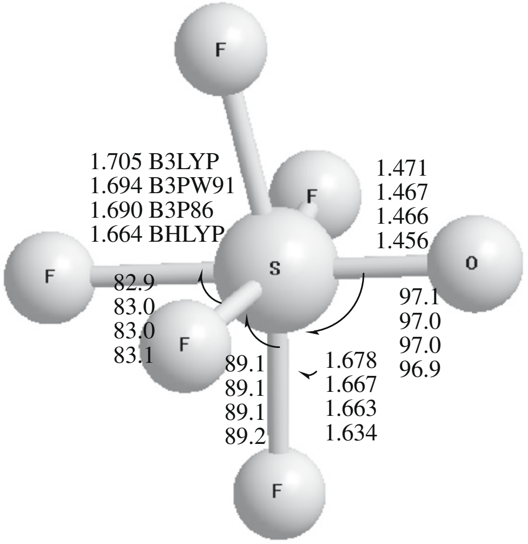
3. Results and discussion

3.1. SF_5O and SF_5O^-

There are a few of previous studies on the structure of the SF_5O. Kronberg et al. [10] have performed a detailed study of SF_5O at B3LYP/6-311++G (3df, 3pd) level in 2005. Our DFT results are C_{2v} symmetry with $^2B_2$ state, shown in Fig. 1. As can be seen from Fig. 1, the bond lengths are predicted to be 1.618–1.634 Å for the S–O bond, 1.568–1.600 Å for the S-F axial (S–F_a) bond, and 1.577–1.611 Å and 1.571–1.606 Å for the two different S–F equatorial (S–F_e) bonds. The bond angles are predicted to be 92.1–92.5° and 88.0–88.3° for the two different bond angle O–S–F_e. It is worthy to note that the geometries predicted using the four functions are all similar, with small variations in bond lengths and angles (on the order of hundredth of angstrom and tenths of degree). The general trend for the bond lengths of SF_5O is B3LYP > B3PW91 > B3P86 > BHLYP. To our knowledge, no experimental geometry parameters have been reported for SF_5O. According to our previous study on geometry parameters of SF_6 substituted species [4], we find that the BHLYP method is an excellent method at predicting the S–F bond length. The bond lengths and bond angles predicted by the BHLYP method are 1.618 Å (the S–O bond), 1.568 Å (the S–F_a bond), 1.571 and 1.577 Å (the S–F_e bond), and 92.1° and 88.3° (the bond angle O–S–F_e), similar to the B3LYP/6-311++G (3df, 3pd) result of Kronberg et al. [10]: 1.612, 1.580, 1.585, and 1.591 Å and 92.4° and 87.6°.



Neutral SF_5O C_{2v} $^2B_2$



Anion SF_5O^- C_{4v} $^1A_1$

Fig. 1. Optimized geometries for the neutral SF_5O and anion SF_5O^- (bond length in angstrom and angles in degree).

For the anion SF_5O^-, the ground state structure has C_{4v} symmetry with $^1A_1$ state (shown in Fig. 1). The bond lengths are evaluated to be 1.456–1.471 Å for the S–O bond, 1.664–1.705 Å for the S–F_a bond, and 1.634–1.678 Å for the S–F_e bond. The bond angle O–S–F_e is in the range of 96.9–97.1°. Our BHLYP results are 1.456 Å (the S–O bond), 1.634 Å (the S–F_a bond), and 1.664 Å (the four equivalent S–F_e bonds), which are similar to the results presented by Arnold et al. [11] at MP2 (full)/6-311+G (d) level: 1.456, 1.707, and 1.676 Å.

IR active harmonic vibrational frequencies and their intensities of SF_5O/SF_5O^- predicted by each functional and the experimental frequency values are available in Table 1. From Table 1, we can see that, the BHLYP method predicts the largest vibrational frequency values, while the B3LYP method gives the smallest