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Rotational spectra of isotopic species of silyl fluoride. Part II: Theoretical and semi-experimental equilibrium structure

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ABSTRACT

The equilibrium structure of silyl fluoride, SiH_3F, has been reinvestigated using both theoretical and experimental data. With respect to the former, quantum-chemical calculations at the coupled-cluster level have been employed together with extrapolation to the basis set limit, consideration of higher excitations in the cluster operator, and inclusion of core correlation as well as relativistic corrections (r(Si–F) = 1.5911 Å, r(Si–H) = 1.4695 Å, and ∠FSiH = 108.30°). A semi-experimental equilibrium structure has been determined based on the available rotational constants for the various isotopic species of silyl fluoride ($^{28}SiH_3F$, $^{28}SiD_3F$, $^{29}SiH_3F$, $^{29}SiD_3F$, $^{30}SiH_3F$, $^{30}SiD_3F$, $^{28}SiH_2DF$, and $^{28}SiHD_2F$) together with computed vibrational corrections to the rotational constants (r(Si–F) = 1.59048(6) Å, r(Si–H) = 1.46948(9) Å, and ∠FSiH = 108.304(9)°).

1. Introduction

A recent investigation of the rotational spectra of three isotopic species of silyl fluoride, namely $^{28}SiH_3F$, $^{29}SiH_3F$, and $^{30}SiH_3F$ [1] provides the possibility to redetermine its equilibrium structure. In an earlier study of the structure of SiH_3F by Boulaftali et al. [2], a slight disagreement between the structural parameters obtained in different ways, i.e., quantum-chemical calculations, experimental and semi-experimental determinations, has been noted and so-called median values have been recommended as the most reliable parameters. The present redetermination of the structure of SiH_3F offers the possibility to resolve this discrepancy and to analyze the origin of the noted discrepancies. For this purpose, both theoretical and experimental data will be exploited; the former are obtained from high-level quantum-chemical calculations and the latter are the ground-state rotational constants available in the literature for eight isotopic species.

With respect to the reported disagreement in Ref. [2], we note that a true experimental structure has been reported based on the rotational constants and vibration–rotation interaction constants for two isotopic species, namely $^{28}SiH_3F$ and $^{28}SiD_3F$. This structure has been compared to a mixed theoretical–experimental structure, derived by correcting the corresponding ground-state rotational constants for the same two isotopologues using computed vibrational corrections, as well as to a pure theoretical structure obtained in high-level quantum-chemical calculations using coupled-cluster techniques. The disagreement among the structures mentioned above is of the order of 0.001–0.002 Å for the two bond distances (r(Si–F) and r(Si–H)) and 0.1–0.3° for the FSiH angle, with the largest discrepancies noted between the experimental structure on one side and the semi-experimental and purely theoretical structure on the other side. The disagreement might be due to inaccuracies in the experimental data used or, though somewhat less likely, due to the restriction to two isotopic species which does not necessarily lead to a balanced description of the structure.

The present investigation exploits the data obtained in a recent experimental study of silyl fluoride using the Lamb-dip technique [1], where significantly improved ground-state rotational constants B_0 have been reported for $^{28}SiH_3F$, $^{29}SiH_3F$, and $^{30}SiH_3F$. These improved constants together with those available for the other isotopic species ($^{28}SiD_3F$, $^{29}SiD_3F$, $^{30}SiD_3F$, $^{28}SiH_2DF$, $^{28}SiHD_2F$, Refs. [3–7]) are used in the determination of a semi-experimental equilibrium structure with the corresponding vibrational corrections obtained in second-order Møller–Plesset perturbation theory and coupled-cluster calculations. With respect to the pure theoretical determination of the equilibrium structure, high-level quantum-chemical calculations at the coupled-cluster level have been performed. By means of an additivity scheme (see Ref. [8] for details) it is possible to extrapolate the results to the one-electron basis-set limit [9] and at the same time to account for higher excitations, core correlation as well as relativistic effects. In these calculations, we are aiming at "quantitative" accuracy thereby providing a conclusive answer concerning the equilibrium geometry of silyl fluoride.

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The paper is organized as follows. In the next section, the methodology used is explained together with the corresponding quantum-chemical details. Thereafter, the results are reported and discussed with an emphasis on a detailed comparison with those reported in Ref. [2].

2. Methodology and computational details

In the present work, most of the calculations have been performed at the coupled-cluster (CC) level of theory [10] employing the CC singles and doubles (CCSD) approximation augmented by a perturbative treatment of triple excitations (CCSD(T)) [11], the full CC singles, doubles and triples (CCSDT) [12], and the CC singles, doubles, triples, quadruples (CCSDTQ) [13] models. All these calculations have been carried out with the quantum-chemical CFOUR program package [14], except those including higher excitations which have been performed with the MRCC package [15] by Kállay interfaced to CFOUR.

2.1. Theoretical equilibrium structure

To reach high accuracy and to account simultaneously for basis-set effects as well as higher excitations and core-correlation effects, the equilibrium geometry of silyl fluoride has been obtained by making use of various composite quantum-chemical schemes [8,9]. In these schemes, the various contributions are evaluated separately at the highest possible level and then combined in order to obtain a best theoretical estimate. In the case of a geometry optimization, this means that the nuclear gradient comprises of various contributions: the Hartree-Fock self-consistent-field (HF-SCF) part extrapolated to the basis-set limit, the valence correlation energy as obtained at the CCSD(T) level extrapolated to the basis-set limit, core-correlation contributions, corrections due to the use of the full CCSDT approach instead of the perturbative CCSD(T) scheme, corrections due to quadruples excitations, and relativistic effects.

The extrapolation to the complete basis set (CBS) limit has been performed as described in Ref. [8], i.e., the CBS gradient is given by

$$\frac{dE_{\mathrm{CBS}}}{dx} = \frac{dE^{\infty}(\mathrm{HF\text{-}SCF})}{dx} + \frac{d\Delta E^{\infty}(\mathrm{CCSD(T)})}{dx}, \tag{1}$$

where $dE^{\infty}(\mathrm{HF-SCF})/dx$ and $d\Delta E^{\infty}(\mathrm{CCSD(T)})/dx$ are the nuclear gradients obtained using an exponential extrapolation for the HF-SCF energy [16] and the n^{-3} extrapolation scheme for the CCSD(T) correlation contribution [17]. The formula given above assumes that Dunning's hierarchy of correlation-consistent valence cc-pVnZ bases [18,19] has been employed: n = Q, 5 and 6 have been chosen for the HF-SCF extrapolation, whereas n = 5 and 6 have been used for CCSD(T), with n denoting the cardinal number of the corresponding basis set. To monitor the convergence to the CBS limit, geometry optimizations at the CCSD(T) level in conjunction with the cc-pVnZ (n = Q, 5, 6) basis sets have also been performed.

Core-correlation effects have been considered in the gradient by adding the corresponding correction, $d\Delta E(\mathrm{core})/dx$, to Eq. (1):

$$\frac{dE_{\mathrm{CBS+core}}}{dx} = \frac{dE^{\infty}(\mathrm{HF\text{-}SCF})}{dx} + \frac{d\Delta E^{\infty}(\mathrm{CCSD(T)})}{dx} + \frac{d\Delta E(\mathrm{core})}{dx}, \tag{2}$$

with the core-correlation energy contribution as difference of all-electron and frozen-core CCSD(T) calculations using the core-valence quintuple-zeta basis set, i.e., the cc-pCV5Z set [20,21].

In a similar manner, corrections due to a full treatment of triples, $d\Delta E(\mathrm{full\text{-}T})/dx$, and quadruples, $d\Delta E(\mathrm{full\text{-}Q})/dx$, have been accounted for and added to Eq. (2):

$$\frac{dE_{\mathrm{CBS+core+fT}}}{dx} = \frac{dE^{\infty}(\mathrm{HF\text{-}SCF})}{dx} + \frac{d\Delta E^{\infty}(\mathrm{CCSD(T)})}{dx} + \frac{d\Delta E(\mathrm{core})}{dx} + \frac{d\Delta E(\mathrm{full\text{-}T})}{dx} \tag{3}$$

and

$$\frac{dE_{\mathrm{CBS+core+fT+fQ}}}{dx} = \frac{dE^{\infty}(\mathrm{HF\text{-}SCF})}{dx} + \frac{d\Delta E^{\infty}(\mathrm{CCSD(T)})}{dx} + \frac{d\Delta E(\mathrm{core})}{dx} + \frac{d\Delta E(\mathrm{full\text{-}T})}{dx} + \frac{d\Delta E(\mathrm{full\text{-}Q})}{dx}. \tag{4}$$

The corresponding differences between CCSDT and CCSD(T) and between CCSDTQ and CCSDT have been obtained in frozen-core calculations employing the cc-pVTZ and cc-pVDZ basis sets, respectively.

Finally, additional contributions due to relativistic effects have been considered. These have been treated using lowest-order direct perturbation theory (second-order in 1/c, DPT2) [22] at the CCSD(T) level together with an uncontracted-cc-pCVQZ (cc-pCVQZ-unc)[1] with all electrons considered in the correlation treatment. The corresponding corrections have been obtained, in analogy to the previous ones, as differences between the CCSD(T)/cc-pCVQZ-unc and DPT2/CCSD(T)/cc-pCVQZ-unc levels and they have been then added at the gradient level in order to obtain our best theoretical estimate:

$$\frac{dE_{tot}}{dx} = \frac{dE^{\infty}(\mathrm{HF-SCF})}{dx} + \frac{d\Delta E^{\infty}(\mathrm{CCSD(T)})}{dx} + \frac{d\Delta E(\mathrm{core})}{dx} + \frac{d\Delta E(\mathrm{full\text{-}T})}{dx} + \frac{d\Delta E(\mathrm{full\text{-}Q})}{dx} + \frac{d\Delta E(\mathrm{DPT2})}{dx}. \tag{5}$$

2.2. Semi-experimental equilibrium structure

The so-called semi-experimental (or empirical) structure of silyl fluoride has been obtained by a least-squares fit of the molecular structural parameters to the equilibrium moments of inertia I_e^i derived from

$$B_e^i = B_0^i + \frac{1}{2}\sum_r \alpha_r^i. \tag{6}$$

The vibrational corrections are here given in terms of the vibration–rotation interaction constants α_r^i, with r denoting the normal mode and i the inertial axis. Note that in Eq. (6) the sum runs over all normal modes and thus the complete set of α_r^i is required to correct the rotational constants for vibrational effects.

The needed vibration–rotation interaction constants have been obtained using quantum-chemical calculations by means of a perturbative approach as described in Ref. [23]. The required harmonic and anharmonic force fields have been computed at the second-order Møller–Plesset perturbation theory (MP2) [24] as well as at the CCSD(T) level using the core-valence polarized cc-pCVTZ basis sets [20,21]. The harmonic force field has been obtained using analytic second-derivative techniques [25], while the corresponding cubic force field has been determined in a normal-coordinate representation via numerical differentiation of the analytically evaluated force constants as described in Refs. [23,26,27]. The cubic force field has been initially obtained for the main isotopic species (i.e., $^{28}SiH_3F$) and the vibrational corrections to the rotational constants have been obtained using the expressions given in Ref. [28]. For the subsequent computations of the vibrational corrections for the other isotopologues, the force fields have not been recalculated but instead obtained by a suitable transformation from the original representation into the normal-coordinate representation of the considered isotopic species.

[1] Note that in the uncontracted basis the additional steep s and p functions of the cc-pCVQZ basis have been skipped to avoid linear dependencies in the calculations.