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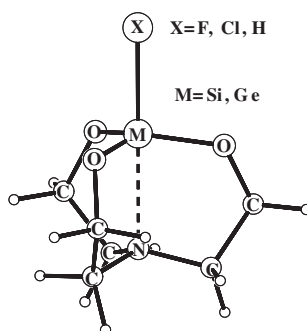
Vibrational spectra of silatranes and germatranes $\text{XM}(\text{OCH}_2\text{CH}_2)_3\text{N}$ ($\text{X} = \text{F}, \text{Cl}, \text{H}$; $\text{M} = \text{Si}, \text{Ge}$). The problem of the theoretical prediction of condensed phase spectra

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HIGHLIGHTS

- ▶ The vibrational spectra are assigned using scaled force fields.
- ▶ Emphasis is placed on the attribution of modes.
- ▶ This involves stretching of the transannular X...N bond.

GRAPHICAL ABSTRACT



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ABSTRACT

The structures of silatranes and germatranes $\text{XM}(\text{OCH}_2\text{CH}_2)_3\text{N}$ ($\text{X} = \text{F}, \text{Cl}, \text{H}$; $\text{M} = \text{Si}, \text{Ge}$) were optimized and their vibrational spectra were calculated at the B3LYP/aug-cc-pVDZ level of theory. Theoretical frequencies of vibrations perpendicular to the C_3 axis (E type) are in good agreement with experimental values, while the axial vibrations (MX and M...N stretchings) demonstrate a significant discrepancy with experimental spectra recorded for the crystalline state. This discrepancy stems from the well-known difference in the MX and M...N bond lengths in gas and solid state. The force constant scaling procedure was used to compensate for this difference. As a result a set of scaling factors was refined for 1-Cl-germatrane (the unique atrane for which the distinction between A and E modes was experimentally established). This set was transferred to the theoretical force fields of other atranes, which provided a fair reproduction of their experimental frequencies. The analysis of the normal modes allowed us to assign the ν M...N mode to bands in the $180\text{--}270\text{ cm}^{-1}$ frequency range, although large contributions of these coordinates are in two other modes in the $450\text{--}500\text{ cm}^{-1}$ and $600\text{--}800\text{ cm}^{-1}$ frequency ranges.

The frequencies of degenerate vibrations (with vectors perpendicular to the C_3 axis) do not depend substantially on the axial atom (X and M) substitution, while those of A-type in the $200\text{--}700\text{ cm}^{-1}$ frequency range vary significantly.

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Introduction

Since the early sixties, when the first silatranes were synthesized and characterized [1–3] numerous studies dealing with these

compounds due their unique reactivity and biological properties have been published (see references in the most comprehensive reviews [4–7]). The prominent feature of silatranes is the presence of transannular bonding between silicon and nitrogen atoms and the major part of the works deal with the strength of this bond, which varies substantially depending on the substituents at silicon and the phase in which the substance is studied. Electron diffraction

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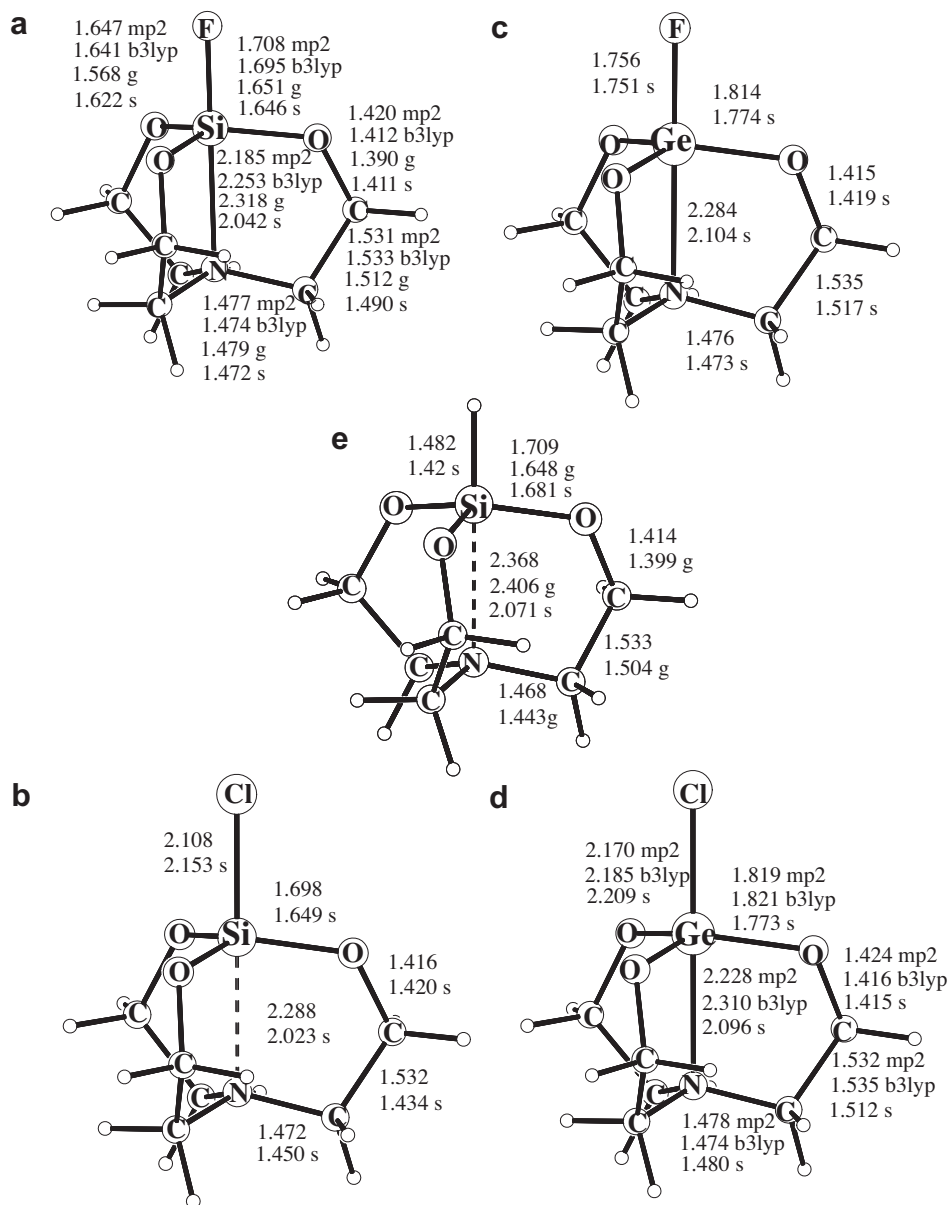


Fig. 1. Equilibrium bond lengths (in Å) optimized at the B3LYP/aug-cc-pVDZ theory level are compared to experimental values (italics) for gas (g) and solid (s) states. For F-silatrane and Cl-germatrane optimized values at the MP2/aug-cc-pVDZ level are added. Experimental data are from references: F-silatrane [9] – g, [12] – s; Cl-silatrane [51] s; F- and Cl-germatrane [49] –s; H-silatrane [10]–g, [13]–s.

studies of gaseous methyl- [8], fluoro- [9] and hydrosilatrane [10] show that the Si...N interatomic distances in the gas phase are by 0.28–0.33 Å longer than in the solid state [11–13].

There exist numerous theoretical studies of silatrane [10,14–32]. The major part of these works deals with the isolated metallo-trane molecules and the equilibrium distances, particularly Si...N separations, obtained in these works, which were published in the last decade, and which employ B3LYP and MP2 methods with basis sets such as 6-311++G**, give a fair agreement with gas electron diffraction data [10]. However, a substantial discrepancy remains between the predicted ab initio Si...N distances and those obtained in the X-ray diffraction studies of the solid state of metallo-tranes. There have been several attempts to compensate this discrepancy by applying the Onsager model [16,17] and by introducing the cluster model to simulate the crystalline state.

In addition to crystallographic studies, a convenient way to characterize metallo-tranes is to analyze their vibrational spectra. Due to the fact that the matter of interest is the strength of the

Si...N transannular interactions there have been several attempts to assign the bands observed in the spectra to this coordinate. In one of the first spectroscopic studies of silatrane [33] the IR band at 570 cm⁻¹ was assigned to the Si...N vibration. However, in later studies based on normal coordinate analysis of silatrane this vibration was assigned to the band in the 350–400 cm⁻¹ range (348 cm⁻¹ for 1-H-silatrane and 398 cm⁻¹ for 1-F-silatrane) [34,35] and to the 468 cm⁻¹ band in the Raman spectrum of 1-hydrosilatrane [36].

Ab initio and DFT methods may provide a fair prediction of vibrational frequencies, especially combined with the scaled quantum mechanical (SQM) force field method [37,38]. However, such results were reported, to the best of our knowledge, only for the 1-hydrosilatrane [10], which have a weak Si...N interaction, compared to the similar distances in halosilatrane. At the B3LYP/6-311++G** level this distance is predicted to be 2.542 Å [10] and the corresponding vibration is assigned to the 184 cm⁻¹ band, observed in the Raman spectrum of polycrystalline powders [34].

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