

Available online at www.sciencedirect.com



Vibrational Spectroscopy 32 (2003) 241-248



www.elsevier.com/locate/vibspec

Calculations of the isotopic shifts of fundamental frequencies for dihaloid silanes

E.N. Chesnokov^{*}, S.R. Gorelik, N.P. Gritsan

Institute of Chemical Kinetics and Combustion, Siberian Branch of the Russian Academy of Sciences, 6300090 Novosibirsk, Russia

Received 27 February 2003; received in revised form 28 May 2003; accepted 2 June 2003

Abstract

Fundamental frequencies of SiH₂F₂ and their isotopic shifts were calculated using ab initio MP2 and QCISD(T) and DFT (B3LYP) methods. The accuracy of calculations was tested by comparison with experimental SiH₂F₂ and SiD₂F₂ frequencies. While most of the fundamental frequencies are predicted very well, the accuracy of calculations of the deuterium isotopic shift was found to be $20-40 \text{ cm}^{-1}$. The most noticeable shift on silicone isotope substitution was found to be $\sim 7 \text{ cm}^{-1}$ for the Si–F stretch mode of B₂ symmetry. Some doubts upon the accuracy of the quantum chemical calculations of the silicone isotopic shifts induced us to find a more accurate method to calculate isotopic shifts. Therefore, the method of analytical calculation of isotopic shifts for the B₁ and B₂ vibration modes of dihaloid silanes was proposed and tested. The results of analytical calculations of the Si–F and Si–Cl stretching vibrations of SiH₂F₂ and SiH₂Cl₂ molecules under isotopic substitution of silicone and chlorine atoms are reported.

© 2003 Elsevier B.V. All rights reserved.

Keywords: Isotopic shift; Fundamental frequencies; Ab initio calculations; Dichlorosilane; Difluorosilane

1. Introduction

It was found recently that the thermal and electric conductivities of the isotopically pure ²⁸Si monocrystals are much higher than those of crystals with a natural isotope composition [1,2]. This finding gives the opportunity of significant improvements of semiconductor technology, which could be particularly important for creating more powerful computer processors.

Silicon has three stable isotopes with a natural composition of 92.2% (²⁸Si), 4.69% (²⁹Si), and

3.09% (³⁰Si). The isotope selective infrared multiphoton dissociation (IR MPD) is one of the most promising methods of silicon isotope separation [2–8]. One of the important factors for successful utilization of this method is an appropriate vibrational isotopic shift. The experimental vibrational isotopic shifts (for silicon isotopes) are known from the literature only for two silicon-containing molecules—SiH₄ [9] and Si₂F₆ [10]. Note that more information is available for the isotopic shifts of the fundamental frequencies during deuteration of silicon containing molecules.

The dihaloid substituted silanes SiH_2F_2 and SiH_2Cl_2 could be one of the most interesting objects for silicone isotopic separation by the IR MPD method because of low activation energy for their dissociation [11,12].

^{*}Corresponding author. Tel.: +7-3832-331322.

E-mail address: chesnok@ns.kinetics.nsc.ru (E.N. Chesnokov).

^{0924-2031/\$ -} see front matter © 2003 Elsevier B.V. All rights reserved. doi:10.1016/S0924-2031(03)00065-1

Recently, the IR MPD of SiH_2F_2 by a CO₂-laser has been studied [13].

According to our knowledge there is no information in the literature on the IR spectra of the silicone isotopically labeled analogues of these molecules. In the absence of experimental data, the IR spectra of parent and isotopically labeled molecules could be calculated by quantum chemistry. Many theoretical methods were tested for the calculations of IR spectra and demonstrated a fairly high accuracy of predictions [14–16].

In this paper, we report the results of quantum chemical calculations for the fundamental frequencies of a SiH_2F_2 molecule and its isotopically substituted analogues. The experimental IR spectra of SiH_2F_2 and perdeuterated compound SiD_2F_2 are known [17,18] and therefore the accuracy of calculations of the isotopic shifts could be tested.

Thereto, we have found that, in some cases, it is possible to calculate analytically isotopic shift for isotopic substitution of any atom if these shifts are known for deuteration. In the present paper, we report also results of the analytical calculations of the isotopic shifts of some frequencies of SiH_2F_2 and SiH_2Cl_2 molecules under isotopic substitution of silicone and chlorine atoms. The analytical approach for isotopic shift calculation was also used in [19].

2. Quantum chemical calculation of the vibrational frequencies of SiH_2F_2 and its isotopically substituted analogues

Geometry of SiH_2F_2 was optimized and the fundamental frequencies were calculated at different levels of theory (the density functional theory with B3LYP combination of exchange and correlation functionals [20], MP2 [21] and QCISD(T) [22] methods) using different basis sets (6-31G^{**}, 6-311G^{**} and Dunning's correlation-consistent basis set cc-pVTZ [23]). All calculations were performed with the Gaussian-98 suite of programs [24].

All of the methods provide a very reasonable geometry of SiH₂F₂. Moreover, more expensive MP2/ccpVTZ and QCISDT/6-31G^{**} procedures have no advantages over much less resource consuming B3LYP/6-31G^{**} method (Table 1). As regards calculations of fundamental frequencies, all methods reproduce experimental values very well. For instance, the linear dependences of the calculated frequencies versus experimental values have high correlation coefficients (0.9997–0.9999). We have chosen the results of the most conventional B3LYP/6-31G^{**} procedure and the data of the MP2 method with a fairly large basis set (cc-pVTZ) as representative (Table 2). The linear dependences in these cases could be expressed in the following way.

B3LYP/6-31G**:

 $\begin{aligned} v_{exp} \ (cm^{-1}) &= (8 \pm 10) + (0.974 \pm 0.008) \times v_{theor} \\ MP2/cc-pVTZ: \\ v_{exp} \ (cm^{-1}) &= (40 \pm 8) + (0.937 \pm 0.006) \times v_{theor} \end{aligned}$

Table 2 shows that according to the calculations, the most appreciable shift on silicone isotope substitution is observed for the Si–F stretch mode of B₂ symmetry (v_8). At the same time, this mode undergoes a moderate isotopic shift on deuteration (21.2 cm⁻¹) and all methods appreciably overestimate this shift.

A SiH₂F₂ molecule has four vibrations of A₁ symmetry ($v_1 - v_4$, Table 2). On deuteration, the v_1 and v_2 modes exhibit a large isotopic shift, which indicates that these vibrations are localized mainly on the Si–H bonds. On the contrary, the v_3 and v_4 frequencies are almost insensitive to the deuteration and this is the indication of their localization on Si–F bonds.

Table 1

Experimental and calculated values of the bond lengths (Å) and bond angles (°) of SiH₂F₂

	Experimental [25]	B3LYP		MP2		QCISD(T) (6-31G**)
		6-31G ^{**}	6-311G ^{**}	6-31G ^{**}	cc-pVTZ	
R _{SiH}	1.471	1.477	1.472	1.464	1.465	1.466
R _{SiF}	1.577	1.600	1.607	1.605	1.590	1.600
/HSiH	112.02	113.54	114.84	113.51	114.34	113.53
∠FSiF	107.93	108.17	107.59	108.28	108.04	108.1

Table 2

Experimental and calculated values of fundamental frequencies and their isotopic shifts

Vibration	Method	$v (cm^{-1})$	$\frac{\nu(H) - \nu(D)}{(cm^{-1})}$	$v(^{28}\text{Si}) - v(^{29}\text{Si})$ (cm ⁻¹)
v ₁ , A ₁ , Si–H stretch Experimental		2245.7	630	
Calculated	Analytic			
Calculated	B3LYP/6-31G ^{**}	2290.8	651.9	0.8
	MP2/cc-pVTZ	2358.7	672.7	0.8
v ₂ , A ₁ , H–Si–H bend Experimental		981.7	274.6	
Calculated	Analytic			
	B3LYP/6-31G**	996	291.0	1.8
	MP2/cc-pVTZ	1012.6	291.2	1.4
v ₃ , A ₁ , Si–F stretch				
Experimental		869.6	8.5	
Calculated	Analytic			
	B3LYP/6-31G**	872.8	-12.9	3.7
	MP2/cc-pVTZ	870.3	-8.0	4.2
v ₄ , A ₁ , F–Si–F bend Experimental		322	5	
Calculated	Analytic			
	B3LYP/6-31G**	316.8	3.8	1.2
	MP2/cc-pVTZ	319.3	3.9	1.2
v ₅ , A ₂ , F–Si–H Experimental		730	198	
Coloulated	Analytia		201.6	0
Calculated	R3I VP/6 31C**	746 4	201.0	0
	MP2/cc-pVTZ	751.1	200.5	0
v_6 , B ₁ , Si–H stretch				
Experimental		2250.5	599.4	
Calculated	Analytic		593.7	2.83
	B3LYP/6-31G**	2299.1	633.7	1.9
	MP2/cc-pVTZ	2367.8	652.7	2.0
v ₇ , B ₁ , SiH ₂ rock				
Experimental		730	151	
Calculated	Analytic		152	2.28
	B3LYP/6-31G**	725	143.6	2.6
	MP2/cc-pVTZ	725	144.2	2.5
v ₈ , B ₂ , Si–F stretch				
Experimental		981	21.2	
Calculated	Analytic		23.6	7.25
	B3LYP/6-31G**	1034.6	42.8	7.0
	MP2/cc-pVTZ	997.1	31.9	7.1

Table 2 (Communed)	Tab	le 2	(Continued)
--------------------	-----	------	-------------

Vibration	Method	$v (\mathrm{cm}^{-1})$	$\frac{v(H) - v(D)}{(cm^{-1})}$	$v(^{28}\text{Si}) - v(^{29}\text{Si})$ (cm ⁻¹)
v ₉ , B ₂ , Si–H wagging Experimental		903.4	223.4	
Calculated	Analytic B3LYP/6-31G ^{**} MP2/cc-pVTZ	915.9 918.3	225.6 216.1 223.7	1.19 1.7 2.0

Assignment of the calculated $v_1 - v_4$ for SiD₂F₂ is not evident. To make this problem clear we performed several calculations with mass of hypothetical hydrogen atom between 1 and 2. These calculations show continuous correlation between v_1 (Si–H stretch) in SiH₂F₂ and SiD₂F₂ molecules. Also we got continuous correlation for v_4 mode (F–Si–F bend). On the contrary, calculations show continuous transformation of v_2 in SiH₂F₂ (H–Si–H bend) to v_3 (Si–F stretch) in SiD₂F₂ molecule. The same behavior we obtained for v_3 mode of SiH₂F₂ (Si–F stretch), which transforms to v_2 (D–Si–D bend) in SiD₂F₂ molecule.

For this assignment we get $v_2(H) - v_2(D) = 291 \text{ cm}^{-1}$ and $v_3(H) - v_3(D) = -12.9$ in a reasonable agreement with experimental values. Note, that negative value of the isotopic shift for v_3 mode does not contradict with the requirement dv/dm < 0 because there is no continuous correlation between SiH₂F₂ and SiD₂F₂ modes.

The molecule has one vibration of A_2 symmetry (v_5), whose isotopic shift is well reproduced by quantum chemical calculations. The values of deuterium isotopic shift for the vibrations of the B_1 and B_2 symmetries are also fairly well reproduced by quantum chemical calculations. In the latter case, however, we observe some tendency to overestimate the degree of delocalization for vibrations with close frequencies (i.e. $v_8 = 981 \text{ cm}^{-1}$ and $v_9 = 903 \text{ cm}^{-1}$ of B_2 symmetry). The isotopic shift calculated for the v_8 appreciably exceeds the experimental value (Table 2).

Thus, it is clear that the isotopic shifts observed on the deuteration of difluorosilane can be calculated with accuracy about 20 cm⁻¹. The most noticeable shift on silicone isotope substitution was found to be $\sim 7 \text{ cm}^{-1}$. Therefore, desired accuracy for silicon isotopic shift is about 1 cm⁻¹. Some doubts upon the accuracy of the quantum chemical calculations of the silicone isotopic shifts induced us to find a more accurate analytical method to calculate isotopic shifts.

3. Analytic calculation of the vibrational frequencies of isotopically substituted SiH₂F₂ and SiH₂Cl₂

The SiH₂F₂ and SiH₂Cl₂ molecules belong to C_{2v} point group and their nine normal modes are distributed over symmetry types as follows: $4A_1 \oplus A_2 \oplus 2B_1$ \oplus 2B₂. The matrices of kinetic and potential energies split into the 4D matrix corresponding to the vibrations of symmetry A₁, the 1D matrix for A₂ vibrations, and two 2D matrices for the vibrations of symmetries B_1 and B_2 . The elements of the kinetic energy matrix are given via atomic masses and geometric parameters of a molecule. Those of the potential energy matrix (which are a combination of molecule force constants) should be determined from the experimental frequencies. It appears that all elements of the potential energy matrix for the vibrations of A₂, B₁ and B₂ symmetries can be determined from the set of experimental frequencies for normal and fully deuterated molecules. Thereafter we can readily calculate vibration frequencies of the molecule containing any combination of isotopes.

For simplicity, the calculations were performed in Cartesian coordinates. As a basis, we have chosen the simultaneous shifts of equivalent atoms with the symmetry required. Fig. 1 shows two deformation types for the molecules with symmetry B_1 .

The vector $Q_1 = ((1,0,0)(1,0,0)(0,0,0)(0,0,0))$ (0,0,0)) describes a simultaneous shift of two halogen atoms in the XZ plane along the X-axis. The vector $Q_2 = ((0,0,0)(0,0,0)(0,0,0)(1,0,0)(1,0,0))$ describes the escape of two hydrogen atoms from the YZ plane toward X. To exclude motion of the center of



Fig. 1. Geometry of the SiH_2X_2 molecule and basis set for B_1 symmetry vibrations.

mass and rotation of the molecule as a whole we use the new basis

 $q_1 = Q_1 + c_1 T + d_1 R;$ $q_2 = Q_2 + c_2 T + d_2 R$

where T = ((1,0,0)(1,0,0)(1,0,0)(1,0,0)(1,0,0))is the vector describing molecule motion along the X-axis, and $\mathbf{R} = ((a \sin(\alpha/2), 0, -a \cos(\alpha/2)))$ $(a \sin(\alpha/2), 0, a \cos(\alpha/2))(0, 0, 0)(-b \cos(\beta/2), 0, 0)$ $(-b \cos(\beta/2), 0, 0))$ is the vector giving molecule rotation about the Y-axis. Letters *a*, *b*, *a*, and *β* denote the lengths of bonds and the angles in-between.

The conditions, under which the linear momentum projection onto the *X*-axis

$$\sum_{i=1}^5 m_i(\boldsymbol{q}_1)_{ix} = 0$$

and the angular momentum projection onto the Y-axis

$$\sum m_i(z_i(\boldsymbol{q}_1)_{ix}-x_i(\boldsymbol{q}_1)_{iz})=0$$

are zero, allow us to determine the coefficients c_1 , c_2 , d_1 , d_2 and thus to find the vectors q_1 and q_2 .

In the basis of q_1 and q_2 vectors, the kinetic energy matrix is of the form

$$\boldsymbol{M}_{nl} = \sum_{i=1}^{5} m_i ((\boldsymbol{q}_n)_{ix} (\boldsymbol{q}_l)_{ix} + (\boldsymbol{q}_n)_{iy} (\boldsymbol{q}_l)_{iy} + (\boldsymbol{q}_n)_{iz} (\boldsymbol{q}_l)_{iz})$$

The potential energy matrix does not change upon transition from Q_1 , Q_2 to q_1 , q_2 . The vibrational frequencies are calculated from the eigenvalues of the square matrix $M^{-1} \cdot K$, where K is the potential energy matrix. Since this is the 2D matrix, the eigenvalues are determined analytically.

The matrix **K** is symmetric and has three different elements k_{11} , k_{22} , and k_{12} . The elements can be determined from the set of the experimental frequencies of

hydrogen- and deuterium-containing molecules using the available four experimental frequencies ${}^{\rm H}\omega_1^{\rm B_1}$, ${}^{\rm H}\omega_2^{\rm B_1}$, ${}^{\rm D}\omega_1^{\rm B_1}$, and ${}^{\rm D}\omega_2^{\rm B_1}$, which is sufficient for unambiguous determination of k_{11} , k_{22} , and k_{12} .

The basis for B₂ symmetry modes were $Q_1 = ((0,1,0)(0,1,0)(0,0,0)(0,0,0)(0,0,0))$ and $Q_2 = ((0,0,0)(0,0,0)(0,0,0)(0,1,0)(0,1,0))$. The calculations were quite similar to that for B₁ symmetry modes.

The calculation results are summarized in Table 3. The second and fourth columns of Table 3 contain the experimental values of the vibrational frequencies for the molecules SiH₂F₂, SiD₂F₂, SiH₂Cl₂, and SiD₂Cl₂ taken from [17,18]. The third and fifth columns include the best results of fitting upon which the elements of the potential energy matrix k_{11} , k_{22} , and k_{12} were varied. Obtained values of the k_{11}, k_{22}, k_{12} are presented also. The structural parameters of molecules (bond lengths and valence angles) were taken from [25,26]. In most cases, all four experimental frequencies were fitted with the accuracy better than 1 cm^{-1} . Using the resulting parameters k_{11} , k_{22} , and k_{12} , we calculated frequencies for molecules with isotopes ²⁹Si and ³⁷Cl. The results are also shown in the third and fifth columns of Table 3.

The accuracy of calculation of the isotopic shifts was determined using calculations, in which the experimental frequencies were varied within some limits. As follows from [27], the accuracy of the experimental frequencies for these molecules is $1-3 \text{ cm}^{-1}$. The calculations indicate that a variation of each experimental frequency by 3 cm^{-1} changes the calculated isotopic shift by less than 0.18 cm⁻¹.

The problem of application of the above method to the vibrations of another symmetry or to the molecules displaying another symmetry is solved as follows.

If a molecule has only one vibration of some symmetry, we can readily derive the analytical expression to describe the dependence of vibration frequency on the masses of atoms, which can be exemplified by the A_2 symmetry vibration of SiH₂F₂ and SiH₂Cl₂ molecules. For this vibration, we get

$$\omega_{\mathrm{A}_2}^2 = \mathrm{const}\left(\frac{1}{m_{\mathrm{H}} \cdot a^2 \cdot \sin^2(\alpha/2)} + \frac{1}{m_{\mathrm{X}} \cdot b^2 \cdot \sin^2(\beta/2)}\right)$$

where $m_{\rm H}$ and $m_{\rm X}$ are the masses of hydrogen and halogen atoms, *a* and *b* are the distances Si-H and

Table 3

Experimental and fitted values of the fundamental frequencies of the B_1 and B_2 symmetry for SiH_2X_2 , SiD_2X_2 and isotopic shifts from analytic calculations

Isotopic composition	v ₆ , Si–H stretching		v ₇ , SiH ₂ rock	
	Experimental	Fitting	Experimental	Fitting
SiH ₂ F ₂ B ₁ symmetry ($k_{11} = 1.23, k_{22} = 4.37, k_{23} = 4.37$	$x_{12} = 1.05$)			
28 SiH ₂ F ₂	2250.5	2250.68	730	730.55
28 SiD ₂ F ₂	1651.1	1650.86	579	578.31
$^{29}\text{SiH}_2\text{F}_2$ (isotopic shift $^{28}\text{Si}{-}^{29}\text{Si}$)		2247.85 (2.83)		728.27 (2.28)
	v ₈ , Si–F stretching	5	v9, Si–H wagging	
SiH ₂ F ₂ B ₂ symmetry ($k_{11} = 7.32, k_{22} = 0.951$,	$k_{12} = -0.498)$			
²⁸ SiH ₂ F ₂	981.7	982.55	903.4	904.33
28 SiD ₂ F ₂	959.8	958.92	680	678.76
29 SiH ₂ F ₂ (isotopic shift 28 Si– 29 Si)		975.30 (7.25)		903.14 (1.19)
	v ₆ , Si–H stretchin	v ₆ , Si–H stretching		
SiH ₂ Cl ₂ B ₁ symmetry ($k_{11} = 0.626, k_{22} = 4.31$	$k_{12} = 0.792$			
²⁸ SiH ₂ Cl ₂	2237	2237.65	602	604.42
²⁸ SiD ₂ ³⁵ Cl ₂	1637	1636.11	466	462.84
²⁹ SiH ₂ ³⁵ Cl ₂ (isotopic shift ²⁸ Si- ²⁹ Si)		2235.03 (2.62)		602.87 (1.53)
²⁸ SiH ₂ ³⁷ Cl ₂ (isotopic shift ³⁵ Cl- ³⁷ Cl)		2237.62 (0.03)		603.85 (0.65)
	v ₈ , Si–Cl stretchir	ıg	v9, Si–H wagging	
SiH ₂ Cl ₂ B ₂ symmetry ($k_{11} = 4.31, k_{22} = 0.849$	$k_{12} = -0.729$			
²⁸ SiH ₂ Cl ₂	590	590.87	876	876.60
²⁸ SiD ₂ ³⁵ Cl ₂	566	565.07	663	662.21
²⁹ SiH ₂ ³⁵ Cl ₂ (isotopic shift ²⁸ Si- ²⁹ Si)		584.34 (6.53)		876.58 (0.02)
²⁸ SiH ₂ ³⁷ Cl ₂ (isotopic shift ³⁵ Cl- ³⁷ Cl)		585.63 (5.24)		874.75 (1.85)

Elements of K matrix are presented in mDin/Å.

Si–X, α and β are the angles H–Si–H and X–Si–X. The frequency ω_{A_2} is independent of the Si atom mass because the atom is not involved in the A₂ vibration.

If there are two vibrations of the same symmetry, the method can be used in the form described for the B_1 and B_2 vibrations of SiH₂F₂ molecules.

Let us consider the case where a molecule has three vibrations of the same symmetry. For example, we can take the SiF₃H molecule with the C_{3v} symmetry, which has three symmetric and three doubly degenerate vibrations, $3A_1 \oplus 3E$. The 3D potential energy matrix has six independent elements. For their determination, we have three experimental frequencies in the normal molecule and three in the deuterated molecule. However, these six frequencies are not independent, and relate to one another via the "rule of products" [28]. Therefore, in this case, the method cannot be used to unambiguously determine the

elements of the potential energy matrix from vibration frequencies. Actually, it can be applied only in case of two modes of the same symmetry.

Finally, we give the calculation results for the frequencies of stretching Si–Cl vibrations in the SiH₂Cl₂ molecule taking into account the presence of various Si and Cl isotopes and the natural ratio between the ³⁵Cl and ³⁷Cl concentrations. This molecule could be interesting object for IRMPD with new IR free electron lasers [8,29]. Fig. 2 displays vibrational frequencies for nine varieties of isotopically labeled dichlorsilane molecules. The height of the column in the figure indicates a relative content of a corresponding isotopic variety. For convenience, the columns corresponding to rare silicon isotopes ²⁹Si and ³⁰Si are magnified 10-fold. As follows from the figure, the possibility of a selective vibrational excitation of dichlorsilane molecules containing various



Fig. 2. Isotopic structure of the v_8 mode of SiH₂Cl₂. Height of the bar represents the natural abundance of each isotopomer. For ²⁹Si and ³⁰Si the bars are 10 times magnified.

silicon isotopes still remains, despite the presence of chlorine isotopes, because most of the heavy chlorine isotopes are in the form of the mixed $Si^{35}Cl^{37}ClH_2$ molecules. For these, the isotopic shift is 2.62 cm⁻¹, which is substantially smaller than the isotopic shift observed upon substitution of silicon isotopes. A fraction of $Si^{37}Cl_2H_2$ molecules whose isotopic shift is close to that for silicon is about 6%.

References

- W.S. Capinski, H.J. Maris, E. Bauser, E. Silier, M. Asen-Palmer, T. Ruf, M. Cardona, E. Gmelin, Appl. Phys. Lett. 71 (1997) 2109.
- [2] K. Takyu, K.M. Itoh, K. Oka, N. Saito, V.I. Ozhogin, J. Appl. Phys. Jpn. 38 (1999) 1493.
- [3] J.L. Lyman, S.D. Rockwood, J. Appl. Phys. 47 (1976) 595.
- [4] N.K. Serdyuk, E.N. Chesnokov, V.N. Panfilov, React. Kinet. Catal. Lett. 17 (1981) 19.
- [5] M. Kamioka, S. Arai, Y. Ishikawa, S. Isomura, N. Takamiya, Chem. Phys. Lett. 119 (1985) 357.
- [6] M. Kamioka, Y. Ishikawa, H. Kaetsu, S. Isomura, S. Arai, J. Phys. Chem. 90 (1986) 5727.
- [7] H. Suzuki, H. Araki, T. Noda, J. Jpn. Inst. Met. 61 (1997) 145.

- [8] J.L. Lyman, B.E. Newman, T. Noda, H. Suzuki, J. Phys. Chem. A 103 (1999) 4227.
- [9] G. Pierre, A. Valentin, L. Heyry, Can. J. Phys. 64 (1986) 341.
- [10] V. Tosa, S. Isomura, Y. Kuga, K. Takeuchi, Vibrat. Spectrosc. 8 (1994) 45.
- [11] M. Koshi, S. Kato, H. Matsui, J. Phys. Chem. 95 (1991) 1223.
- [12] P. Ho, M.E. Coltrin, J.S. Binkley, C.F. Melius, J. Phys. Chem. 89 (1985) 4647.
- [13] S.R. Gorelik, L.V. Kuibida, E.N. Chesnokov, R.R. Akberdin, A.K. Petrov, Infrared multiphoton dissociation of difluorosilane, Appl. Phys. B, 2003, in press.
- [14] B.G. Johnson, P.M.W. Gill, J.A. Pople, J. Chem. Phys. 98 (1993) 5612.
- [15] C. Adamo, V. Barone, J. Chem. Phys. 108 (1998) 664.
- [16] C.J. Cramer, Essentials of Computational Chemistry: Theories and Models, Wiley, Baffins Lane, 2002, p. 300.
- [17] S. Cradock, E.A.V. Ebsworth, A.G. Robiette, Trans. Faraday Soc. 60 (1964) 1502.
- [18] D.H. Christensen, O.F. Nielsen, J. Mol. Spectrosc. 27 (1968) 489.
- [19] C.V. Sheth, Spectrochim. Acta 44A (1988) 683.
- [20] (a) A.D. Becke, J. Chem. Phys. 98 (1993) 5648;
 (b) C. Lee, W. Yang, R.G. Parr, Phys. Rev. B 37 (1988) 785.
- [21] M.J. Frisch, M. Head-Gordon, J.A. Pople, Chem. Phys. Lett. 166 (1990) 275, 281.

- [22] (a) J. Cizek, Adv. Chem. Phys. 14 (1969) 35;
 (b) G.D. Purvis, R.J. Bartlett, J. Chem. Phys. 76 (1982) 1910;
 (c) G.E. Scuseria, H.F. Schaefer Jr., J. Chem. Phys. 90 (1989)
 - 3700.
- [23] D.E. Woon, T.H. Dunning, J. Chem. Phys. 98 (1993) 1358.
- [24] M.J. Frisch et al., Gaussian-98, Revision A.6-A11, Gaussian, Inc., Pittsburgh, PA, 1998.
- [25] V.W. Laurie, J. Chem. Phys. 26 (1956) 1359.
- [26] R.W. Davis, M.C. Gerry, J. Mol. Spectrosc. 60 (1976) 117.
- [27] T. Shimanouchi, J. Phys. Chem. Ref. Data 6 (1972) 993.
- [28] E.B. Wilson Jr., J.E. Decius, P.E. Cross, Molecular Vibrations, McGraw-Hill, New York, 1955.
- [29] A.K. Petrov, E.N. Chesnokov, S.R. Gorelik, K.D. Straub, J.M.J. Madey, E.B. Szarmes, J. Phys. Chem. A 101 (1997) 7200.