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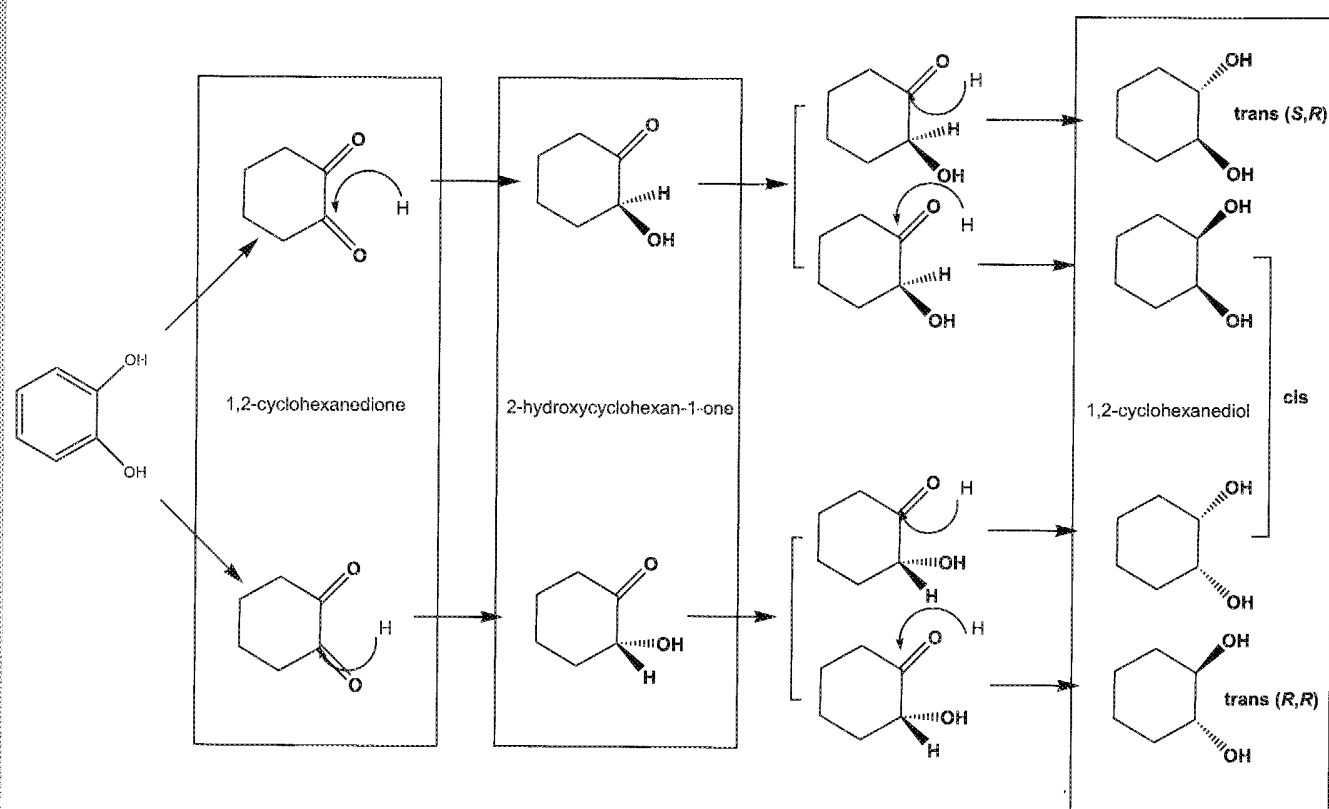
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# Scaled quantum mechanical force fields for trifluoromethyl selenium derivatives. I. The $\text{CF}_3\text{SeCN}$ and $\text{CF}_3\text{SeCH}_3$ molecules

L.E. Fernández and E.L. Varetti

**Abstract:** Force fields and vibrational properties were calculated for the trifluoromethyl selenium derivatives,  $\text{CF}_3\text{SeCN}$  and  $\text{CF}_3\text{SeCH}_3$ , by means of density functional theory (DFT) techniques. The existing experimental data and assignments for these molecules were confirmed by the theoretical results. These data were subsequently used in the definition of scaled quantum mechanical force fields for such chemical species. The obtained force constants are compared with results previously published for similar compounds.

**Key words:** trifluoromethyl selenium, force constants, structure, DFT calculation.

**Résumé :** Faisant appel à des techniques de la théorie de la fonctionnelle de densité (« DFT »), on a calculé les champs de force et les propriétés vibrationnelles de dérivés trifluorométhylsélénium, soit le  $\text{CF}_3\text{SeCN}$  et le  $\text{CF}_3\text{SeCH}_3$ . Les données expérimentales et les attributions pour ces composés ont été confirmées par les résultats théoriques. On a subséquemment utilisé ces données dans la définition d'un champ de force normalisé en mécanique quantique pour de telles espèces. On a comparé les constantes de force obtenues avec les résultats publiés antérieurement pour des composés semblables.

**Mots clés :** trifluorométhylsélénium, constantes de force, calculs selon la théorie de la fonctionnelle de densité.

[Traduit par la Rédaction]

## Introduction

A theoretical study of the vibrational properties of the selenium compounds,  $\text{CF}_3\text{SeX}$  ( $\text{X} = \text{H}$ ,  $\text{D}$ ,  $\text{Cl}$ , or  $\text{Br}$ ), was recently performed in our laboratory (1). Similar calculations are now made on other two simple  $\text{CF}_3\text{Se}$  derivatives, i.e.,  $\text{CF}_3\text{SeCN}$  and  $\text{CF}_3\text{SeCH}_3$ . These molecules were prepared from  $(\text{CF}_3\text{Se})_2\text{Hg}$  by Dale et al. (2) and by Emeléus and Welchman (3). The molecular parameters for  $\text{CF}_3\text{SeCN}$  were obtained by the electron diffraction method (4), but no structural study is known for the  $\text{CF}_3\text{SeCH}_3$  molecule. IR and Raman spectra were reported for these two molecules by Marsden (5) and by Clase et al. (6), and normal coordinate analyses were also published (7).

In the present work, quantum chemical calculations were performed on the mentioned molecules to obtain the corresponding force constants, which were scaled to reproduce

the experimental frequencies. Such adjustment was made using the formalism of the scaled quantum mechanical (SQM) force field, as defined by Pulay et al. (8).

## Calculation procedure

Optimized structures and vibrational wavenumbers for  $\text{CF}_3\text{SeCN}$  and  $\text{CF}_3\text{SeCH}_3$  were obtained with density functional theory (DFT) methods using the B3LYP functional (9, 10) together with the 6-311G\* basis set. This theoretical data facilitated the comparison of the results with those obtained in previous work in which the same combination of functional and basis sets was used. The natural bond orbitals (NBO) formalism (11) was used for the calculation of the atomic charges, which appear in Fig. 1. The calculations were made with the Gaussian 98 set of programs (12).

## Structural results

The molecular conformations of the two molecules were investigated starting with initial, staggered structures having  $\text{FCSeC}$  dihedral angles of  $180^\circ$ . The respective  $\text{CF}_3$  group was rotated around the  $\text{Se}-\text{C}$  bond from  $0^\circ$  to  $60^\circ$ , in steps of  $5^\circ$ , and the structure was optimized with that dihedral angle frozen. These calculations showed that only a single conformer exists for both compounds, corresponding to the structures of symmetry  $\text{C}_s$  shown in Fig. 1. The potential energy curve shows maxima for structures in which the trifluoromethyl group is rotated  $60^\circ$  with respect to the most stable conformation.

An additional series of calculations were performed for the  $\text{CF}_3\text{SeCH}_3$  molecule in which the  $\text{CF}_3$  and  $\text{CH}_3$  groups

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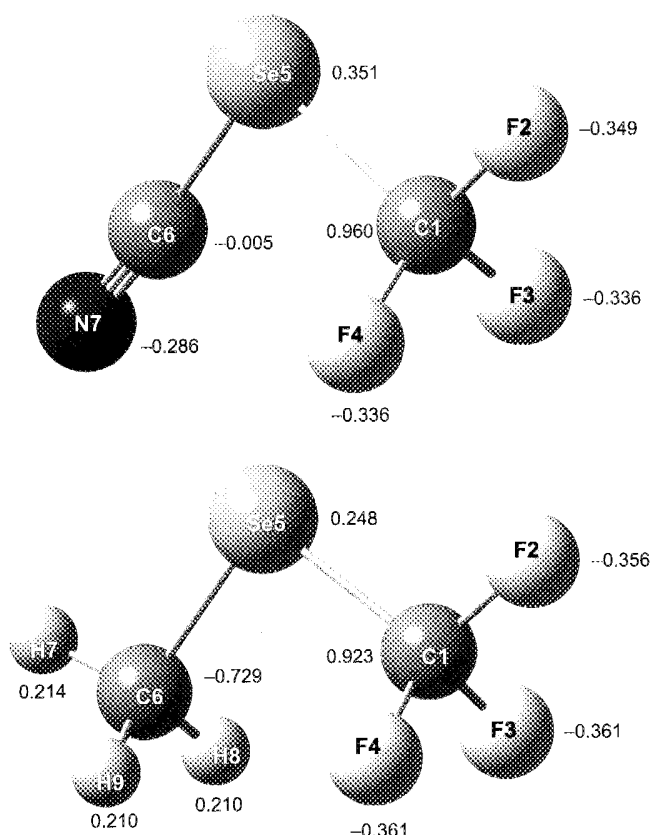
**L.E. Fernández.** Instituto de Química y Física, Facultad de Bioquímica, Química y Farmacia, Universidad Nacional de Tucumán, San Lorenzo 456, 4000 S.M. de Tucumán, República Argentina.

**E.L. Varetti.**<sup>1,2</sup> Centro de Química Inorgánica (CEQUINOR, CONICET-UNLP), Departamento de Química, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, C. Correo 962, 1900 La Plata, República Argentina.

<sup>1</sup>Member of the Carrera del Investigador Científico, CONICET, República Argentina.

<sup>2</sup>Corresponding author (e-mail: varetti@quimica.unlp.edu.ar).

**Fig. 1.** The calculated molecular structure and atomic charges for the molecules  $\text{CF}_3\text{SeCN}$  and  $\text{CF}_3\text{SeCH}_3$ .



were rotated simultaneously in the same or opposite directions in steps of  $10^\circ$ . These calculations confirmed the existence of only one minimum in the potential energy surface.

The most stable conformations predicted for these molecules were fully optimized, and their structures are shown in Fig. 1. As mentioned before, structural geometrical parameters were reported only for  $\text{CF}_3\text{SeCN}$  (4), and these values are shown in Table 1 together with the calculated values. The (mean) calculated and experimental distances and angles do not differ by more than  $0.020 \text{ \AA}$  and  $3.4^\circ$ , respectively. The theoretical tilt angles existing between the C–Se bonds and the ideal symmetry axis of the  $\text{CX}_3$  group, with  $\text{X} = \text{F}$  or  $\text{H}$ , also appear in Table 1; this angle is calculated for the  $\text{CF}_3$  groups as  $1/3[2\alpha(\text{F3,4–C–Se}) - 2\alpha(\text{F2–C–Se})]$  (13). Clearly,  $\text{CF}_3\text{SeCN}$  shows a tilt angle that is considerably larger than those calculated for  $\text{SeCF}_3$  and  $\text{SeCH}_3$  in  $\text{CF}_3\text{SeCH}_3$ . This theoretical result could be explained by taking into account the calculated electric charges on the atoms. In fact, the F3, F4, and N7 atoms of  $\text{CF}_3\text{SeCN}$  (Fig. 1) show negative charges of  $-0.34$  (F) and  $-0.29$  (N); whereas, in  $\text{CF}_3\text{SeCH}_3$  the charges are positive for H8 and H9 ( $+0.21$ ) and negative for F3 and F4 ( $-0.36$ ). Therefore, the repulsive forces between the F and N atoms in the former molecule could explain the relatively large tilt angle of the  $\text{SeCF}_3$  moiety and the predicted value of  $176.6^\circ$  for the Se–C–N angle; whereas, the attractive forces between the mentioned H and F atoms in the latter molecule could be the cause of the notably smaller calculated tilt angles.

**Table 1.** Optimized geometric parameters for the molecules  $\text{CF}_3\text{SeCN}$  and  $\text{CF}_3\text{SeCH}_3$  and experimental data for  $\text{CF}_3\text{SeCN}$ .

	$\text{CF}_3\text{SeCN}$		$\text{CF}_3\text{SeCH}_3$
	Calculated	Experimental (4)	Calculated
<b>Bond lengths (<math>\text{\AA}</math>)</b>			
C1–F2	1.339	1.332	1.342
C1–F3,4	1.33	—	1.346
Se– $\text{CF}_3$	2.004	1.984	1.968
Se–CN	1.846	1.854	—
C≡N	1.157	1.152	—
Se– $\text{CH}_3$	—	—	1.971
C6–H7	—	—	1.089
C6–H8,9	—	—	1.087
<b>Bond angles (<math>^\circ</math>)</b>			
F3–C1–F4	108.6	109.4	106.7
F2–C1–F3,4	109.1	—	108.1
F2–C1–Se5	105.6	109.6	108.7
F3,4–C1–Se5	112.2	—	112.6
Tilt Se– $\text{CF}_3$	4.37	—	2.62
C–Se–C	95.6	92.2	95.4
Se–C–N	176.6	180.0 (fixed)	—
H8–C6–H9	—	—	111.1
H7–C6–H8,9	—	—	109.8
H7–C6–Se5	—	—	106.1
H8,9–C6–Se5	—	—	110.0
Tilt Se– $\text{CH}_3$	—	—	2.55

## Vibrational results

The normal modes of vibration of the  $\text{CF}_3\text{SeCN}$  and  $\text{CF}_3\text{SeCH}_3$  molecules, with Cs symmetry, are classified as  $10A' + 5A''$  and  $13A' + 8A''$ , respectively.

The atomic displacements calculated for each vibrational mode, represented graphically with the program Moldraw (14), confirmed the assignment of bands proposed by Clase et al. (6) for both molecules. In fact, these authors corrected and completed a previous study made on  $\text{CF}_3\text{SeCN}$  and related molecules by Marsden (5). The experimental wavenumbers for each molecule reported in ref. 6 appear in Tables 2 and 3 together with the corresponding qualitative intensities. In most cases, the observed values agree with the calculated IR and Raman band intensities. That agreement is particularly clear for the bands due to the  $\text{CF}_3$  stretching vibrations where the strongly polarized C–F bonds produce very strong IR bands and weak or very weak Raman bands. The agreement between measured and calculated wavenumbers was evaluated by means of the root-mean-square deviation (RMSD), which was equal to  $29 \text{ cm}^{-1}$  for  $\text{CF}_3\text{SeCN}$  and  $55 \text{ cm}^{-1}$  for  $\text{CF}_3\text{SeCH}_3$ . After the force field scaling procedure, these values fell to 8 and  $7 \text{ cm}^{-1}$ , respectively.

## Force constants

The force fields in Cartesian coordinates, as generated by the Gaussian programs for the two molecules, were transformed to the set of non-redundant coordinates defined in Tables 4 and 5. Such coordinates consider the local symmetry of the  $\text{CF}_3$  and  $\text{CH}_3$  groups and follow the proposals of Fogarasi et al. (15). The resulting force constants were sub-

**Table 2.** Experimental and calculated wavenumbers, IR and Raman intensities and, potential energy distribution (PED) for CF<sub>3</sub>SeCN.

Mode	Experimental (6) <sup>a</sup>	Calcd. <sup>b</sup>	Calcd. SQM <sup>c</sup>	IR intensity (km mol <sup>-1</sup> )	Raman intensity (Å <sup>4</sup> (amu) <sup>-1</sup> )	PED (contributions ≥ 10%)	Main coordinate
<b>A'</b>							
v <sub>1</sub>	2178 (s)	2274	2185	2.14	109.75	95 S <sub>1</sub>	v(C≡N)
v <sub>2</sub>	1201 vs. (vvw)	1190	1196	225.92	0.73	101 S <sub>2</sub> + 19 S <sub>5</sub>	v(CF <sub>3</sub> ) antisymm.
v <sub>3</sub>	1103 vs. (vw)	1079	1090	523.6	5.89	76 S <sub>3</sub> + 49 S <sub>4</sub> + 22 S <sub>8</sub>	v(CF <sub>3</sub> ) symm.
v <sub>4</sub>	747 vs. (vs)	742	752	32.83	6.79	47 S <sub>4</sub> + 31 S <sub>3</sub> + 14 S <sub>8</sub>	δ(CF <sub>3</sub> ) symm.
v <sub>5</sub>	543 (m)	551	553	1.14	0.77	50 S <sub>5</sub> + 22 S <sub>6</sub>	δ(CF <sub>3</sub> ) antisymm.
v <sub>6</sub>	534 s (m)	534	536	3.08	3.38	72 S <sub>6</sub> + 19 S <sub>5</sub>	v(Se-C(N))
v <sub>7</sub>	390 m (vvw)	402	397	2.46	0.94	37 S <sub>7</sub> + 11 S <sub>5</sub> + 24 S <sub>10</sub>	δ(SeCN) in plane
v <sub>8</sub>	315 m (vs)	300	316	1.1	6.86	66 S <sub>8</sub> + 11 S <sub>4</sub>	v((F <sub>3</sub> )C-Se)
v <sub>9</sub>	272 vw (m)	267	267	0.57	3.01	84 S <sub>9</sub> + 23 S <sub>7</sub>	ρ(CF <sub>3</sub> )
v <sub>10</sub>	118 (m)	98	97	3.77	3.29	78 S <sub>10</sub> + 32 S <sub>7</sub> + 19 S <sub>9</sub>	δ(CSeC)
<b>A''</b>							
v <sub>11</sub>	1197 vs	1199	1205	270.59	0.61	102 S <sub>11</sub> + 18 S <sub>12</sub>	v(CF <sub>3</sub> ) antisymm.
v <sub>12</sub>	—	529	532	1.44	0.99	77 S <sub>12</sub>	δ(CF <sub>3</sub> ) antisymm.
v <sub>13</sub>	356 w (vvw)	359	344	1.35	1.88	98 S <sub>13</sub>	δ(SeCN) out of plane
v <sub>14</sub>	282 (vvw)	273	275	0.03	1.16	96 S <sub>14</sub> + 11 S <sub>12</sub>	ρ(CF <sub>3</sub> )
v <sub>15</sub>	—	33	34	1.49	1.24	103 S <sub>15</sub>	Torsion (CF <sub>3</sub> )
RMSD (cm <sup>-1</sup> )	29	8					

<sup>a</sup>Qualitative intensities for IR and Raman (in parentheses) observed bands: w, weak; m, medium; s, strong; v, very.<sup>b</sup>B3LYP/6-311G\* calculations.<sup>c</sup>From SQM force field.**Table 3.** Experimental and calculated wavenumbers, IR and Raman intensities, and potential energy distribution (PED) for CF<sub>3</sub>SeCH<sub>3</sub>.

Mode	Experimental (6) <sup>a</sup>	Calcd. <sup>b</sup>	Calcd. SQM <sup>c</sup>	IR intensity (km mol <sup>-1</sup> )	Raman intensity (Å <sup>4</sup> (amu) <sup>-1</sup> )	PED (contributions ≥ 10%)	Main coordinate
<b>A'</b>							
v <sub>1</sub>	3035 w (w)	3161	3039	3.38	56.62	100 S <sub>1</sub>	v(CH <sub>3</sub> ) antisymm.
v <sub>2</sub>	2955 s (s)	3069	2950	13.33	113.22	100 S <sub>2</sub>	v(CH <sub>3</sub> ) symm.
v <sub>3</sub>	1438 s	1497	1440	12.32	7.81	96 S <sub>3</sub>	δ(CH <sub>3</sub> ) antisymm.
v <sub>4</sub>	1288 vs	1337	1284	11.39	0.36	105 S <sub>4</sub>	δ(CH <sub>3</sub> ) symm.
v <sub>5</sub>	1157 vs	1161	1167	241.27	0.8	96 S <sub>5</sub> + 18 S <sub>10</sub>	v(CF <sub>3</sub> ) antisymm.
v <sub>6</sub>	1117 vs (vw)	1097	1106	438.34	1.28	70 S <sub>6</sub> + 49 S <sub>8</sub> + 24 S <sub>11</sub>	v(CF <sub>3</sub> ) symm.
v <sub>7</sub>	916	939	903	17.36	3.76	88 S <sub>7</sub>	ρ(CH <sub>3</sub> )
v <sub>8</sub>	740 vs (s)	735	742	15.64	4.29	42 S <sub>8</sub> + 35 S <sub>6</sub> + 12 S <sub>11</sub>	δ(CF <sub>3</sub> ) symm.
v <sub>9</sub>	597	577	599	0.68	20.64	107 S <sub>9</sub>	v(Se-CH <sub>3</sub> )
v <sub>10</sub>	533 w (vw)	538	541	0.29	1.22	73 S <sub>10</sub>	δ(CF <sub>3</sub> ) antisymm.
v <sub>11</sub>	339 s (ms)	331	338	2.15	4.12	53 S <sub>11</sub> + 13 S <sub>8</sub> + 11 S <sub>12</sub>	v(Se-CF <sub>3</sub> )
v <sub>12</sub>	302 m (m)	295	298	0.6	3.41	61 S <sub>12</sub> + 18 S <sub>11</sub> + 11 S <sub>10</sub>	ρ(CF <sub>3</sub> )
v <sub>13</sub>	148 (m)	156	150	1.82	1.28	95 S <sub>13</sub> + 33 S <sub>12</sub>	δ(CSeC)
<b>A''</b>							
v <sub>14</sub>	3036 w (w)	3172	3050	3.38	56.62	100 S <sub>14</sub>	v(CH <sub>3</sub> ) antisymm.
v <sub>15</sub>	1431 s (vw)	1484	1427	6.31	10.49	95 S <sub>15</sub>	δ(CH <sub>3</sub> ) antisymm.
v <sub>16</sub>	1141 vs	1133	1140	263.8	0.7	100 S <sub>16</sub> + 19 S <sub>18</sub>	v(CF <sub>3</sub> ) antisymm.
v <sub>17</sub>	911	934	897	4.63	3.43	95 S <sub>17</sub>	ρ(CH <sub>3</sub> )
v <sub>18</sub>	536	526	529	0.55	0.95	73 S <sub>18</sub>	δ(CF <sub>3</sub> ) antisymm.
v <sub>9</sub>	289 (w)	283	285	0	1.19	94 S <sub>19</sub> + 13 S <sub>18</sub>	ρ(CF <sub>3</sub> )
v <sub>20</sub>	—	129	129	0.04	0.03	108 S <sub>20</sub>	Torsion (CH <sub>3</sub> )
v <sub>21</sub>	—	51	49	0.87	1.17	106 S <sub>21</sub>	Torsion (CF <sub>3</sub> )
RMSD (cm <sup>-1</sup> )	55	7					

<sup>a</sup>Qualitative intensities for IR and Raman (in parentheses) observed bands: w, weak; m, medium; s, strong; v, very.<sup>b</sup>B3LYP/6-311G\* calculations.<sup>c</sup>From SQM force field.

**Table 4.** Natural internal (local symmetry) coordinates for  $\text{CF}_3\text{SeCN}$ .

Definition (according to Fig. 1)	Description <sup>a</sup>
<b>A'</b>	
$S_1 = d(6-7)$	$\nu(\text{C}\equiv\text{N})$
$S_2 = 2r(1-2) - r(1-3) - r(1-4)$	$\nu(\text{CF}_3)$ antisymm.
$S_3 = r(1-2) + r(1-3) + r(1-4)$	$\nu(\text{CF}_3)$ symm.
$S_4 = \alpha(2-1-3) + \alpha(2-1-4) + \alpha(3-1-4) - \beta(2-1-5) - \beta(3-1-5) - \beta(4-1-5)$	$\delta(\text{CF}_3)$ symm.
$S_5 = 2\alpha(3-1-4) - \alpha(2-1-3) - \alpha(2-1-4)$	$\delta(\text{CF}_3)$ antisymm.
$S_6 = l(5-6)$	$\nu(\text{Se-CN})$
$S_7 = \delta(5-6-7)$	$\delta(\text{SeCN})$ in plane
$S_8 = t(1-5)$	$\nu(\text{Se-CF}_3)$
$S_9 = 2\beta(2-1-5) - \beta(3-1-5) - \beta(4-1-5)$	$\rho(\text{CF}_3)$
$S_{10} = \gamma(1-5-6)$	$\delta(\text{CSeC})$
<b>A''</b>	
$S_{11} = r(1-3) - r(1-4)$	$\nu(\text{CF}_3)$ antisymm.
$S_{12} = \alpha(2-1-3) - \alpha(2-1-4)$	$\delta(\text{CF}_3)$ antisymm.
$S_{13} = \delta(5-6-7)$	$\delta(\text{SeCN})$ out of plane
$S_{14} = \beta(3-1-5) - \beta(4-1-5)$	$\rho(\text{CF}_3)$
$S_{15} = \Sigma\tau[\text{Fi-C1-Se5-C6}]$	Torsion ( $\text{CF}_3$ )

<sup>a</sup>v, stretching;  $\delta$ , deformation;  $\rho$ , rocking.**Table 5.** Natural internal (local symmetry) coordinates for  $\text{CF}_3\text{SeCH}_3$ .

Definition (according to Fig. 1)	Description <sup>a</sup>
<b>A'</b>	
$S_1 = 2d(7-6) - d(8-6) - d(9-6)$	$\nu(\text{CH}_3)$ antisymm.
$S_2 = d(7-6) + d(8-6) + d(9-6)$	$\nu(\text{CH}_3)$ symm.
$S_3 = 2\psi(8-6-9) - \psi(8-6-7) - \psi(9-6-7)$	$\delta(\text{CH}_3)$ antisymm.
$S_4 = \psi(7-6-9) + \psi(7-6-8) + \psi(8-6-9) - \phi(7-6-5) - \phi(8-6-5) - \phi(9-6-5)$	$\delta(\text{CH}_3)$ symm.
$S_5 = 2r(1-2) - r(1-3) - r(1-4)$	$\nu(\text{CF}_3)$ antisymm.
$S_6 = r(1-2) + r(1-3) + r(1-4)$	$\nu(\text{CF}_3)$ symm.
$S_7 = 2\phi(7-6-5) - \phi(8-6-5) - \phi(9-6-5)$	$\rho(\text{CH}_3)$
$S_8 = \alpha(2-1-3) + \alpha(4-1-2) + \alpha(4-1-3) - \beta(2-1-5) - \beta(3-1-5) - \beta(4-1-5)$	$\delta(\text{CF}_3)$ symm.
$S_9 = l(6-5)$	$\nu(\text{Se-CH}_3)$
$S_{10} = 2\alpha(3-1-4) - \alpha(3-1-2) - \alpha(4-1-2)$	$\delta(\text{CF}_3)$ antisymm.
$S_{11} = t(1-5)$	$\nu(\text{Se-CF}_3)$
$S_{12} = 2\beta(2-1-5) - \beta(3-1-5) - \beta(4-1-5)$	$\rho(\text{CF}_3)$
$S_{13} = \delta(1-5-6)$	$\delta(\text{CSeC})$
<b>A''</b>	
$S_{14} = d(8-6) - d(9-6)$	$\nu(\text{CH}_3)$ antisymm.
$S_{15} = \psi(8-6-7) - \psi(9-6-7)$	$\delta(\text{CH}_3)$ antisymm.
$S_{16} = r(1-3) - r(1-4)$	$\nu(\text{CF}_3)$ antisymm.
$S_{17} = \phi(8-6-5) - \phi(9-6-5)$	$\rho(\text{CH}_3)$
$S_{18} = \alpha(3-1-2) - \alpha(4-1-2)$	$\delta(\text{CF}_3)$ antisymm.
$S_{19} = \beta(3-1-5) - \beta(4-1-5)$	$\rho(\text{CF}_3)$
$S_{20} = \Sigma\tau[\text{Hi-C6-Se5-C1}]$	Torsion ( $\text{CH}_3$ )
$S_{21} = \Sigma\tau[\text{Fi-C1-Se5-C6}]$	Torsion ( $\text{CF}_3$ )

<sup>a</sup>v, stretching;  $\delta$ , deformation;  $\rho$ , rocking.

sequently scaled according to the scheme of Pulay et al. (8), in which the main force constants are multiplied by scale factors (e.g.,  $f_i$  and  $f_j$ ), and the corresponding interaction constants are multiplied by  $(f_i \times f_j)^{1/2}$ , adjusting the scale factors to reproduce the experimental wavenumbers as accurately as possible.

The final scaling factors corresponding to each force constant for the two studied species appear in Table 6. Obviously, most of these factors are greater than one. This is the case when heavy atoms (after the second row of the Periodic Table) appear in the molecule. This fact has been reported for many molecules containing non-metallic heavy atoms

**Table 6.** Final scaling factors for the force field of the molecules  $\text{CF}_3\text{SeCN}$  and  $\text{CF}_3\text{SeCH}_3$ .

Coordinates <sup>a</sup>	$\text{CF}_3\text{SeCN}$	$\text{CF}_3\text{SeCH}_3$
$\nu(\text{CF}_3)$ , $\delta(\text{CF}_3)$ , $\rho(\text{CF}_3)$ , Torsion ( $\text{CF}_3$ )	1.011	1.013
$\nu(\text{Se-CN})$	1.011	—
$\nu(\text{Se-CH}_3)$	—	1.075
$\nu(\text{Se-CF}_3)$	1.155	1.075
$\nu(\text{CH}_3)$ , $\delta(\text{CH}_3)$ , $\rho(\text{CH}_3)$	—	0.924
$\delta(\text{CSeC})$	1.011	0.924
$\nu(\text{C}\equiv\text{N})$ , $\delta(\text{SeCN})$	0.919	—
Torsion ( $\text{CH}_3$ )	—	1.013

<sup>a</sup> $\nu$ , stretching;  $\delta$ , deformation;  $\rho$ , rocking.**Table 7.** Symmetry force constants for the molecule  $\text{CF}_3\text{SeCN}$ .

Force constant <sup>a</sup>	This work	Reference (7)
F1,1	17.321	16.982
F2,2	5.348	5.259
F3,3	7.833	7.461
F4,4	1.639	1.733
F5,5	1.518	1.584
F6,6	3.526	3.452
F7,7	0.24	0.332
F8,8	2.583	2.482
F9,9	0.884	0.83
F10,10	0.973	0.828
F11,11	5.416	5.259
F12,12	1.454	1.584
F13,13	0.311	0.332
F14,14	0.85	0.83
F15,15	0.012	—
F3,8	0.675	0.393
F4,8	-0.437	-0.434
F5,6	-0.016	0.061
F3,4	0.64	0.65
F2,5	-0.63	-0.5
F1,7	0.021	-0.5
F2,9	0.547	0.5
F1,11	0	0.5

<sup>a</sup>Units are  $\text{mdyn } \text{\AA}^{-1}$  (1  $\text{dyn} = 10 \mu\text{N}$ ) for stretchings and stretch-stretch interactions,  $\text{mdyn } \text{\AA}$  for bend and bend-bend interactions, and  $\text{mdyn}$  for stretch-bend interactions.

(16) as well as for several  $\text{CF}_3\text{SO}_2\text{X}$  molecules (17). To prove that the scaling factors are transferable between related molecules, a subsequent calculation was performed using the mean factors for common coordinates previously obtained for the  $\text{CF}_3\text{SeX}$  series (1) and adjusting only the factors that affect the non-common coordinates. In that calculation, the final RMSD values did not differ by more than  $1 \text{ cm}^{-1}$  from those obtained with the scaling factors of Table 6.

The main force constants in symmetry coordinates as well as some interaction constants for the studied molecules are reproduced in Tables 7 and 8 together with the correspond-

**Table 8.** Symmetry force constants for the molecule  $\text{CF}_3\text{SeCH}_3$ .

Force constant <sup>a</sup>	This work	Reference (7)
F1,1	4.96	4.9
F2,2	5.057	4.834
F3,3	0.519	0.514
F4,4	0.527	0.588
F5,5	5.103	4.83
F6,6	7.471	7.461
F7,7	0.546	0.58
F8,8	1.633	1.792
F9,9	2.746	2.642
F10,10	1.574	1.549
F11,11	2.742	2.714
F12,12	0.9	0.93
F13,13	0.916	0.663
F14,14	4.976	4.9
F15,15	0.507	0.514
F6,11	0.628	0.221
F8,11	-0.405	-0.566
F6,8	0.655	0.65
F5,10	-0.645	-0.5
F2,1	-0.014	-0.5
F5,12	0.514	0.5
F2,4	0.13	0.5
F9,4	-0.35	-0.261
F1,3	-0.135	-0.041
F16,15	-0.011	-0.041
F16,16	4.898	4.83
F17,17	0.545	0.58
F18,18	1.502	1.549
F19,19	0.905	0.93
F20,20	0.011	—
F21,21	0.017	—

<sup>a</sup>Units are  $\text{mdyn } \text{\AA}^{-1}$  (1  $\text{dyn} = 10 \mu\text{N}$ ) for stretchings and stretch-stretch interactions,  $\text{mdyn } \text{\AA}$  for bend and bend-bend interactions, and  $\text{mdyn}$  for stretch-bend interactions.

ing values calculated by Wahi et al. (7). Clearly, no large differences appear between both sets of main force constants, based in the same vibrational band assignments. However, there are significant disagreements between the sets of interaction constants, probably because most of these values were fixed in the traditional procedure of refinement performed by these authors. On the other hand, the theoretical approach used in the present work produces a complete force constants matrix. The SQM matrices are available as supplementary data.<sup>3</sup> The SQM force fields were used to calculate the potential energy distributions (PED) that appear in Tables 2 and 3. The PED show that some coordinates are strongly mixed in both molecules, as is the case with  $S_3$  ( $\nu(\text{CF}_3)$  symm.),  $S_4$  ( $\delta(\text{CF}_3)$  symm.), and  $S_8$  ( $\nu(\text{C-Se})$ ) for  $\text{CF}_3\text{SeCN}$  and the corresponding  $S_6$ ,  $S_8$ , and  $S_{11}$  coordinates for  $\text{CF}_3\text{SeCH}_3$ , which appear to be contributing in different proportions to the modes  $\nu_3$  and  $\nu_4$  for the first

<sup>3</sup>Supplementary data for this article are available on the journal Web site or may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0S2, Canada. DUD 5112. For more information on obtaining material, refer to [http://cisti-icist.nrc-cnrc.gc.ca/irm/unpub\\_e.shtml](http://cisti-icist.nrc-cnrc.gc.ca/irm/unpub_e.shtml).

**Table 9.** Internal force constants for CF<sub>3</sub>SeCN, CF<sub>3</sub>SeCH<sub>3</sub>, and the related molecules CF<sub>3</sub>SeX.

Force constant <sup>a</sup>	This work		Reference (1)			
	CF <sub>3</sub> SeCN	CF <sub>3</sub> SeCH <sub>3</sub>	CF <sub>3</sub> SeH	CF <sub>3</sub> SeD	CF <sub>3</sub> SeCl	CF <sub>3</sub> SeBr
<b>Bond stretchings</b>						
<i>f</i> (C–F) <sup>b</sup>	6.167	5.841	5.928	6.004	6.033	5.976
<i>f</i> (Se–CF <sub>3</sub> )	2.583	2.742	2.8	2.84	2.529	2.69
<i>f</i> (Se–CN)	3.526	—	—	—	—	—
<i>f</i> (C≡N)	17.321	—	—	—	—	—
<i>f</i> (Se–CH <sub>3</sub> )	—	2.746	—	—	—	—
<i>f</i> (C–H) <sup>b</sup>	—	4.996	—	—	—	—
<i>f</i> (C–F/C–F) <sup>b</sup>	0.802	0.789	0.826	0.844	0.824	0.818
<i>f</i> (C–F/Se–CF <sub>3</sub> )	0.39	0.362	0.387	0.392	0.364	0.372
<i>f</i> (C–H/CH) <sup>b</sup>	—	0.032	—	—	—	—
<i>f</i> (Se–CN/CN)	0.199	—	—	—	—	—
<b>Deformations</b>						
<i>f</i> (F–C–F) <sup>b</sup>	1.269	1.304	1.305	1.291	1.295	1.252
<i>f</i> (F–C–Se) <sup>b</sup>	0.854	0.874	0.931	0.936	0.845	0.868
<i>f</i> (C–Se–C)	0.973	0.916	—	—	—	—
<i>f</i> (Se–C≡N)	0.24	—	—	—	—	—
<i>f</i> (H–C–H) <sup>b</sup>	—	0.431	—	—	—	—
<i>f</i> (H–C–Se) <sup>b</sup>	—	0.452	—	—	—	—

<sup>a</sup>Units are mdyn Å<sup>-1</sup> (1 dyn = 10 μN) for stretchings and stretch–stretch interactions and mdyn Å rad<sup>-2</sup> (1 dyn = 10 μN) (1 rad = 10 mGy) for angular deformations.

<sup>b</sup>Mean values.

molecule and  $v_6$  and  $v_8$  for the latter. A similar observation was made for the CF<sub>3</sub>SeX molecules (1).

The internal force constants calculated from the corresponding SQM force fields for these molecules are shown in Table 9. As expected, these force constants are close to the values previously obtained for other selenium derivatives using the same calculation procedure (1).

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## References

1. L.E. Fernández and E.L. Varetti. *J. Mol. Struct.: THEOCHEM.* **761**, 217 (2006).
2. J.W. Dale, H.J. Emeléus, and R.N. Haszeldine. *J. Chem. Soc.* 2939 (1958).
3. H.J. Emeléus and N. Welchman. *J. Chem. Soc.* 1268 (1963).
4. C.J. Marsden and G.M. Sheldrick. *J. Mol. Struct.* **10**, 413 (1971).
5. C.J. Marsden. *J. Fluorine Chem.* **5**, 401 (1975).
6. H.J. Clase, P.K. Wahi, and D.R.L. Bomford. *Can. J. Spectrosc.* **22**, 92 (1977).
7. P.K. Wahi and N.D. Patel. *Can. J. Spectrosc.* **22**, 88 (1977).
8. P. Pulay, G. Fogarasi, G. Pongor, J.E. Boggs, and A. Vargha. *J. Am. Chem. Soc.* **105**, 7037 (1983).
9. A.D. Becke. *J. Chem. Phys.* **98**, 5648 (1993).
10. C. Lee, W. Yang, and R.G. Parr. *Phys. Rev. B*, **37**, 785 (1988).
11. A.E. Reed, L.A. Curtiss, and F. Weinhold. *Chem. Rev.* **88**, 899 (1988).
12. M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery, Jr., R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, A.G. Baboul, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, J.L. Andres, C. Gonzalez, Head-M. Gordon, E.S. Replogle, and J.A. Pople. GAUSSIAN 98 [computer program]. Revision a.7. Gaussian, Inc., Pittsburgh, PA. 1998.
13. J.S. Francisco. *Spectrochim. Acta*, **40A**, 923 (1984).
14. P. Uglieri, D. Viterbo, and G. Chiari. *Z. Kristallogr.* **207**, 9 (1993).
15. G. Fogarasi, X. Zhou, P.W. Taylor, and P. Pulay. *J. Am. Chem. Soc.* **114**, 8191 (1992).
16. F. Kalincsák and G. Pongor. *Spectrochim. Acta*, **58A**, 999 (2002).
17. L.E. Fernández, A. Ben Altabef, and E.L. Varetti. *J. Mol. Struct.* **612**, 1 (2002).