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Theoretical potential scans and vibrational spectra of vinyl selenonyl halides $\text{CH}_2=\text{CH}-\text{SeO}_2\text{X}$ (X is F, Cl and Br)

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Abstract The structure and conformational stability of vinyl selenonyl fluoride, chloride and bromide $\text{CH}_2=\text{CH}-\text{SeO}_2\text{X}$ (X is F, Cl and Br) were investigated using density functional B3LYP/6-311+G** and ab initio MP2/6-311+G** calculations. From the calculations the molecules were predicted to exist only in the non-planar *gauche* conformation with the vinyl C=C group almost eclipsing one of the selenonyl Se=O bonds as a result of conjugation between the two moieties. Single-minimum potential scans were calculated at the DFT level for the molecules. The vibrational frequencies were computed using B3LYP/6-311+G**. Normal coordinate calculations were then carried out and potential energy distributions were calculated for the three molecules in the *gauche* conformation.

Keywords Ab initio · Normal coordinate analyses · Vibrational assignment and spectra · Vinyl selenonyl fluoride · Chloride and bromide

Introduction

The conformational behavior and structure of propenoyl halides $\text{CH}_2=\text{CH}-\text{CXO}$ and their halo and methyl derivatives have been of interest for many years. [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12] The conjugation effects generally stabilize the planar *s-cis* and *s-trans* forms and lead to high rotational barriers in these molecules as compared to their saturated analogs.

In propenoyl halides both the halogen and the oxygen atoms of the carbonyl group play a competitive role in determining the conformational equilibrium that leads to a small energy difference between the stable conformers of the molecules. In the case of 2-fluoropropenoyl fluoride [7, 11] and 2-chloropropenoyl fluoride, [8] the *s-*

trans conformer with the two halogen atoms directed away from each other was determined to be more favorable than the *s-cis* form. Furthermore, the presence of the methyl group was shown to influence the direction of the conformational equilibrium in the methyl substituted propenoyl halides significantly. For 2-methyl-2-butenoyl fluoride and chloride the *s-trans* form was found to be the lower energy conformer, while for 3-methyl-2-butenoyl fluoride and chloride the *s-cis* form was determined to be the low-energy conformer. [12, 13]

Sulfones are other important chemicals of interesting structure and applications. [14, 15] Their reactivity in organic synthesis as building blocks in the drug industry [14] earlier led us to investigate the conformational behavior and structural stability of vinyl sulfonyl halides $\text{CH}_2=\text{CH}-\text{SO}_2\text{X}$ [15] and the corresponding selenium derivatives $\text{CH}_2=\text{CH}-\text{SeO}_2\text{X}$ (X=F and Cl) in the present study. In these molecules the conjugation effects between the vinyl C=C moiety and the two S=O (or Se=O) bonds will certainly lead to different conformational stabilities, in which the non-planar *gauche* form may be stabilized in addition to the planar *cis* and *trans* conformers.

Therefore, we have investigated the conformational behavior and structural stability of vinyl selenonyl fluoride, chloride and bromide in the present work. We carried out ab initio optimization of the energies for all the stable conformers and the transition states of the molecules. From the data the relative conformational stability and the barrier to internal rotation were determined. Additionally, vibrational frequencies were calculated and a complete assignment was made for all the normal modes by employing normal coordinate calculations. We also used the vibrational data to make plots for the vibrational IR and Raman spectra of the molecules. The results of this work are presented herein.

Ab initio calculations

The Gaussian 98 program [16] running on an IBM RS/6000 43P model 260 workstation, was used to carry out

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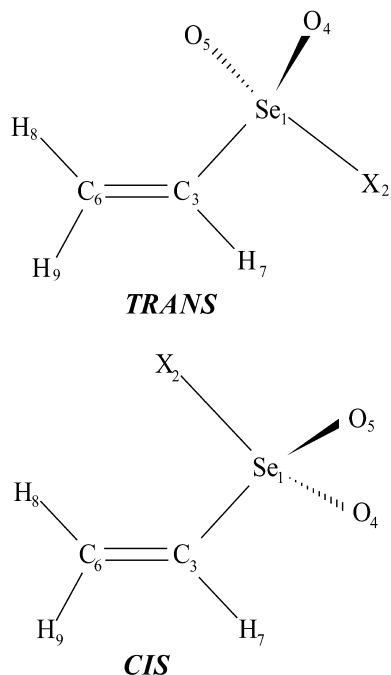


Fig. 1 Atom numbering of vinyl selenonyl halides in the *trans* (upper) and the *cis* (lower) conformation

the LCAO-MO-SCF calculations at the DFT-B3LYP/6-311+G** and ab initio MP2/6-311+G** levels. We optimized the structures of vinyl selenonyl fluoride, chloride and bromide in their possible stable conformations (Fig. 1) by minimizing the energy with respect to all the geometrical parameters. The calculated structural parameters, total energies, rotational constants and dipole moments of the three molecules are listed in Table 1. From the calculations the molecules were found to exist predominantly in the *gauche* conformation with the vinyl C=C group nearly eclipsing one of the selenonyl Se=O bonds as a result of a noticeable conjugation between the two moieties.

Asymmetric torsional potential function

The potential-surface scan for the internal rotation about the C–Se single bond was obtained by allowing the CC–SeX dihedral angle (φ) to vary in 15° increments from 0° (*cis* position) to 180° (*trans* position). Full geometry optimizations at each of the fixed CCSeX dihedral angles (φ) of 15°, 30°, 45°, 75°, 90°, 105°, 135°, 150° and 165° were carried out at the DFT-B3LYP/6-311+G** level of calculations. The potential function for the internal rotation in the three vinyl selenonyl halides was consistent with one minimum at the *gauche* position, as shown in Fig. 2.

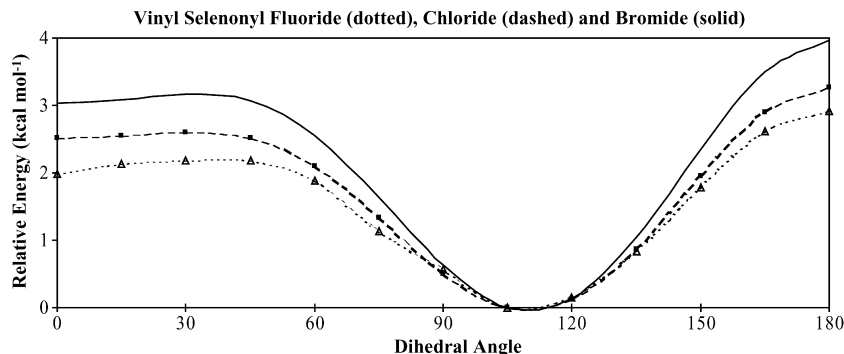
Table 1 Calculated structural parameters, total dipole moment, and rotational constants at DFT-DFT-B3LYP/6-311+G** and MP2/6-311+G** levels of the *gauche* conformation of vinyl selenonyl fluoride (X=F), chloride (X=Cl) and bromide (X=Br)

Parameter ^{a,b}	Fluoride		Chloride		Bromide	
	DFT	MP2	DFT	MP2	DFT	MP2
Bond length (Å)						
$r(\text{Se}_1\text{-X}_2)$	1.803	1.791	2.249	2.210	2.412	2.380
$r(\text{Se}_1\text{-C}_3)$	1.926	1.896	1.935	1.902	1.938	1.906
$r(\text{Se}_1\text{=O}_4)$	1.613	1.598	1.620	1.604	1.623	1.607
$r(\text{Se}_1\text{=O}_5)$	1.611	1.597	1.619	1.603	1.622	1.606
$r(\text{C}_3\text{=C}_6)$	1.323	1.336	1.323	1.336	1.322	1.336
$r(\text{C}_3\text{-H}_7)$	1.082	1.085	1.082	1.085	1.082	1.085
$r(\text{C}_6\text{-H}_8)$	1.084	1.086	1.084	1.086	1.084	1.086
$r(\text{C}_6\text{-H}_9)$	1.085	1.086	1.085	1.086	1.085	1.086
Bond angle (degree)						
$(\text{C}_3\text{Se}_1\text{X}_2)$	96.7	95.9	99.5	98.3	100.3	98.8
$(\text{O}_4\text{Se}_1\text{X}_2)$	105.6	105.5	107.1	106.7	107.6	107.3
$(\text{O}_5\text{Se}_1\text{X}_2)$	104.8	104.7	106.1	106.0	106.7	106.7
$(\text{C}_6\text{C}_3\text{Se}_1)$	118.8	118.6	118.7	118.6	118.8	118.6
$(\text{C}_6\text{C}_3\text{H}_7)$	128.4	127.1	128.5	127.3	128.5	127.5
$(\text{C}_3\text{C}_6\text{H}_8)$	121.8	121.3	121.8	121.2	121.7	121.2
$(\text{C}_3\text{C}_6\text{H}_9)$	120.1	120.0	120.1	120.0	120.1	120.1
$(\text{C}_3\text{X}_2\text{Se}_1\text{O}_4)$	113.7	113.3	113.7	113.3	113.7	113.3
$(\text{C}_3\text{X}_2\text{Se}_1\text{O}_5)$	-113.8	-113.4	-113.6	-113.1	-113.5	-112.9
$(\text{C}_6\text{C}_3\text{Se}_1\text{X}_2)$	107.8	110.1	109.6	109.1	110.0	108.8
Dipole moment (Debye)						
(μ_t)	5.4	6.0	5.1	5.7	5.0	5.6
Rotational constants (MHz)						
<i>A</i>	3,751	3,809	2,621	2,655	2,426	2,478
<i>B</i>	2,173	2,215	1,792	1,856	1,123	1,167
<i>C</i>	2,139	2,177	1,489	1,537	966	998

^a Calculated total energies of the *gauche* conformer of the fluoride, the chloride and the bromide at DFT-B3LYP/6-311+G** level are -2729.811489, -3090.172852 and -5204.099490 hartrees, respectively

^b Calculated total energies of the *gauche* conformer of the fluoride, the chloride and the bromide at MP2/6-311+G** level are -2727.396563, -3087.376046 and -5200.229333 hartrees, respectively

Fig. 2 Potential function for the asymmetric torsion in vinyl selenonyl fluoride (dotted line), chloride (dashed line) and bromide (solid line) as determined at the DFT-B3LYP/6-311+G** level



Vibrational frequencies and normal coordinate analyses

Vinyl selenonyl halides in the *gauche* conformation have C_1 symmetry. The 21 vibrational modes span the irreducible representation 21A and should be polarized in the Raman spectra of the liquid. Normal coordinate analyses were carried out for the stable *gauche* conformer of the three molecules in order to provide a complete assignment of the fundamental vibrational frequencies. A computer program was written for this purpose following Wilson's method. [17] The Cartesian coordinates for the stable conformers together with the normal modes (in Cartesian coordinates) and the frequencies from the Gaussian 98 output were used as input. A complete set of internal coordinates (Table 2) was used to form symmetry coordinates (Table 3).

Table 2 Internal coordinate definitions^a for vinyl selenonyl fluoride (X=F), chloride (X=Cl) and bromide (X=Br)

No.	Coordinate	Definition
1	Se ₁ -X ₂	Stretch T
2	Se ₁ -C ₃	Stretch Q
3	Se ₁ -O ₄	Stretch X ₁
4	Se ₁ -O ₅	Stretch X ₂
5	C ₃ -C ₆	Stretch R
6	C ₃ -H ₇	Stretch S
7	C ₆ -H ₈	Stretch P ₁
8	C ₆ -H ₉	Stretch P ₂
9	C ₃ Se ₁ X ₂	Bend θ
10	O ₄ Se ₁ X ₂	Bend π_1
11	O ₄ Se ₁ C ₃	Bend π_2
12	O ₅ Se ₁ X ₂	Bend ϵ_1
13	O ₅ Se ₁ C ₃	Bend ϵ_2
14	O ₄ Se ₁ O ₅	Bend δ
15	C ₆ C ₃ Se ₁	Bend β_1
16	Se ₁ C ₃ H ₇	Bend β_2
17	C ₆ C ₃ H ₇	Bend β_3
18	H ₈ C ₆ H ₉	Bend α_1
19	C ₃ C ₆ H ₈	Bend α_2
20	C ₃ C ₆ H ₉	Bend α_3
21	CH	Bend ω
22	(H ₈ C ₆ C ₃ Se ₁ -H ₉ C ₆ C ₃ Se ₁)	Torsion ξ_1
23	(H ₈ C ₆ C ₃ Se ₁ +H ₉ C ₆ C ₃ Se ₁)	Torsion ξ_2
24	(X ₂ Se ₁ C ₃ C ₆ O ₄ Se ₁ C ₃ C ₆ O ₅ Se ₁ C ₃ C ₆)	Asymmetric torsion τ

The normal modes were next transformed to mass-weighted Cartesian coordinates, which were then used to calculate the force constant matrix. This was diagonalized and its eigenvectors and eigenvalues were used in the further calculations. Following this step the force-constant matrix was transformed to internal coordinates. To ensure correctness, this transformation was checked numerically in both directions.

At this point the force constant matrix in internal coordinates could be scaled if desired, back-transformed to mass-weighted cartesians and diagonalized again to get scaled frequencies and normal modes. The matrix was finally transformed to symmetry coordinates where again all possible numerical checks were performed.

In the next step the normal modes were also transformed to symmetry coordinates. Finally, the potential energy distribution (PED) for each normal mode among the symmetry coordinates of the three molecules in the *gauche* conformations was calculated and is given in Tables 4, 5 and 6.

A complete assignment of the fundamentals was proposed. The assignments were made based on calculated PED, infrared band intensities, Raman line activities, depolarization ratios, and on those reported for propenoyl chloride and fluoride. [6] The data of the vibrational assignments are listed in Tables 4, 5 and 6.

Calculation of vibrational spectra

To calculate the Raman spectra we used the wavenumbers ν_j , the scattering activities S_j , and the depolarization ratios ρ_j as calculated at the DFT-B3LYP/6-311+G** level. Then the Raman cross-sections ($\partial\sigma_j/\partial\Omega$), which are proportional to the intensities [18, 19] are given as:

$$\frac{\partial\sigma_j}{\partial\Omega} = \frac{(2^4\pi^4/45)(\nu_o - \nu_j)^4 (h/8\pi^2c\nu_j) S_j [(1 - \rho_j)/(1 + \rho_j)]}{1 - \exp(-h\nu_j/k_B T)}$$

Since we use only relative intensities, we calculated them as:

$$I_j = (\partial\sigma_j/\partial\Omega) / (\partial\sigma_{jm}/\partial\Omega)$$

Table 3 Symmetry coordinates for vinyl selenonyl halides in the *gauche* conformation

Species	Description	Symmetry coordinate ^a
A	C–H	$S_1=S$
	CH ₂	$S_2=P_1-P_2$
	CH ₂	$S_3=P_1+P_2$
	SeO ₂	$S_4=X_1+X_2$
	C–Se	$S_5=Q$
	Se–X	$S_6=T$
	C=C	$S_7=R$
	CH ₂	$S_8=2\alpha_1-\alpha_2-\alpha_3$
	CH ₂	$S_9=\alpha_2-\alpha_3$
	SeO ₂	$S_{10}=\epsilon_1-\epsilon_2+\pi_1-\pi_2$
	SeO ₂	$S_{11}=4\delta-\epsilon_1-\epsilon_2-\pi_1-\pi_2$
	CSeX	$S_{12}=5\theta-\epsilon_1-\epsilon_2-\pi_1-\pi_2-\delta$
	CCSe	$S_{13}=2\beta_1-\beta_2-\beta_3$
	CH	$S_{14}=\beta_2-\beta_3$
	SeO ₂	$S_{15}=X_1-X_2$
	SeO ₂	$S_{16}=\epsilon_1+\epsilon_2-\pi_1-\pi_2$
	SeO ₂	$S_{17}=\epsilon_1-\epsilon_2-\pi_1+\pi_2$
	CH	$S_{18}=\omega$
	CH ₂	$S_{19}=\xi_1$
	CH ₂	$S_{20}=\xi_2$
		$S_{21}=\tau$

^a Not normalized**Table 4** Calculated vibrational frequencies (cm⁻¹) at B3LYP/6-311+G** level for the *gauche* conformer of vinyl selenonyl fluoride^a

Sym	No.	Freq.	IR int.	Raman act.	Depol. ratio	PED
A	ν_1	3,235	4.3	73.4	0.4	91% CH ₂ antisym. str. (S ₂)
	ν_2	3,215	3.4	93.7	0.3	89% C–H str. (S ₁)
	ν_3	3,140	1.8	130.1	0.2	98% CH ₂ sym. str. (S ₃)
	ν_4	1,652	0.1	18.2	0.0	78% C=C str. (S ₇)
	ν_5	1,409	20.3	19.6	0.3	19% CH ₂ deformation (scissor) (S ₈) 81% CH ₂ deformation (scissor) (S ₈)
	ν_6	1,246	10.9	5.2	0.2	17% C=C str. (S ₇) 73% CH bend (S ₁₄) 23% CH ₂ wag (S ₉)
	ν_7	1,021	46.3	0.5	0.8	98% CH ₂ def. I (S ₁₉)
	ν_8	1,007	14.0	1.6	0.7	63% CH ₂ wag (S ₉) 23% CH bend (S ₁₄)
	ν_9	976	104.2	14.0	0.7	93% SeO ₂ antisym. str. (S ₁₉)
	ν_{10}	964	12.1	0.3	0.7	67% CH bend (S ₁₈) 30% CH ₂ def. II (S ₂₀)
	ν_{11}	905	64.3	31.1	0.1	98% SeO ₂ sym. str. (S ₄)
	ν_{12}	595	105.3	5.0	0.4	45% CH ₂ def. II (S ₂₀) 25% Se–F str. (S ₆) 20% CH bend (S ₁₈)
	ν_{13}	579	25.4	6.6	0.3	55% C–Se str. (S ₅) 11% CCSe bend (S ₁₃) 10% Se–F str. (S ₆)
	ν_{14}	569	39.1	13.9	0.0	62% Se–F str. (S ₆) 14% C–Se str. (S ₅) 11% CH ₂ def. II (S ₂₀)
	ν_{15}	385	28.8	4.0	0.3	36% CCSe bend (S ₁₃) 21% SeO ₂ rock (S ₁₀) 19% SeO ₂ wag (S ₁₆) 11% C–Se str. (S ₅)
	ν_{16}	323	44.6	9.2	0.5	46% SeO ₂ def. (scissor) (S ₁₁) 19% SeO ₂ rock (S ₁₀) 13% C–Se str. (S ₅)
	ν_{17}	302	16.2	2.7	0.7	50% SeO ₂ rock (S ₁₀) 38% SeO ₂ def. (scissor) (S ₁₁)
	ν_{18}	274	11.2	3.9	0.6	48% SeO ₂ twist (S ₁₇) 36% SeO ₂ wag (S ₁₆)
	ν_{19}	193	0.9	3.3	0.8	77% CSeF bend (S ₁₂)
	ν_{20}	173	0.6	2.3	0.6	44% SeO ₂ twist (S ₁₇) 28% SeO ₂ wag (S ₁₆) 27% CCSe bend (S ₁₃)
	ν_{21}	88	0.2	4.2	0.7	100% asym. torsion (S ₂₁)

^a IR intensities and Raman activities are calculated in Km mol⁻¹ and Å⁴ amu⁻¹, respectively

Table 5 Calculated vibrational frequencies (cm^{-1}) at B3LYP/6-311+G** level for the *gauche* conformer of vinyl selenonyl chloride^a

Sym	No.	Freq.	IR int.	Raman act.	Depol. ratio	PED
A	ν_1	3,232	4.2	84.4	0.5	90% CH ₂ antisym. str. (S ₂)
	ν_2	3,213	3.0	87.6	0.3	89% C–H str. (S ₁)
	ν_3	3,137	1.7	152.0	0.2	98% CH ₂ sym. str. (S ₃)
	ν_4	1,649	0.5	18.5	0.0	78% C=C str. (S ₇)
	ν_5	1,408	19.1	22.7	0.3	18% CH ₂ deformation (scissor) (S ₈) 82% CH ₂ deformation (scissor) (S ₈)
	ν_6	1,240	15.6	7.9	0.2	17% C=C str. (S ₇) 71% CH bend (S ₁₄)
	ν_7	1,017	45.1	0.4	0.7	24% CH ₂ wag (S ₉) 97% CH ₂ def. I (S ₁₉)
	ν_8	1,001	6.4	2.9	0.7	62% CH ₂ wag (S ₉) 25% CH bend (S ₁₄)
	ν_9	959	26.7	3.2	0.6	60% CH bend (S ₁₈) 28% CH ₂ def. II (S ₂₀)
	ν_{10}	956	81.6	12.8	0.7	10% SeO ₂ antisym. str. (S ₁₅) 86% SeO ₂ antisym. str. (S ₁₅)
	ν_{11}	887	69.2	31.7	0.1	99% SeO ₂ sym. str. (S ₄)
	ν_{12}	589	48.7	2.9	0.7	61% CH ₂ def. II (S ₂₀) 32% CH bend (S ₁₈)
	ν_{13}	568	10.4	10.7	0.1	71% C–Se str. (S ₅) 15% CCSe bend (S ₁₃)
	ν_{14}	385	64.3	2.6	0.7	31% CCSe bend (S ₁₃) 24% SeO ₂ rock (S ₁₀)
	ν_{15}	354	63.0	15.6	0.1	17% Se–Cl str. (S ₆) 11% C–Se str. (S ₅) 50% Se–Cl str. (S ₆)
	ν_{16}	309	34.8	13.5	0.3	31% SeO ₂ def. (scissor) (S ₁₁) 51% SeO ₂ def. (scissor) (S ₁₁) 15% SeO ₂ rock (S ₁₀)
	ν_{17}	277	5.2	12.0	0.5	12% C–Se str. (S ₅) 56% SeO ₂ rock (S ₁₀) 24% Se–Cl str. (S ₆)
	ν_{18}	216	4.6	3.6	0.7	12% SeO ₂ def. (scissor) (S ₁₁) 51% SeO ₂ wag (S ₁₆)
	ν_{19}	179	0.6	3.7	0.6	36% SeO ₂ twist (S ₁₇) 57% SeO ₂ twist (S ₁₇) 20% CCSe bend (S ₁₃)
	ν_{20}	161	1.6	3.5	0.7	17% SeO ₂ wag (S ₁₆) 70% CSeCl bend (S ₁₂)
	ν_{21}	85	0.1	6.6	0.7	11% asym. torsion (S ₂₁) 86% asym. torsion (S ₂₁) 13% CSeCl bend (S ₁₂)

^a IR intensities and Raman activities are calculated in Km mol^{-1} and $\text{\AA}^4 \text{amu}^{-1}$, respectively

where jm denotes the normal mode having the largest Raman cross-section. As laser wavelength we took $\lambda_0=514.5 \text{ nm}$ ($\nu_0=1/\lambda_0$), which corresponds to an argon-ion laser. We assumed the temperature to be $T=300 \text{ K}$.

Then the line shapes are calculated as Lorentzians (L) with a width of $\Delta\nu=12 \text{ cm}^{-1}$. Thus, the final spectrum is calculated as:

$$I(\nu) = \sum_j I_j L(\nu - \nu_j)$$

$$L(\nu - \nu_j) = (1/\pi)(\Delta\nu/2) / \left[(\nu - \nu_j)^2 + (\Delta\nu/2)^2 \right]$$

$$\int_{-\infty}^{+\infty} L(\nu) d\nu = 1$$

where j runs over all normal modes. For the plots we used a grid of step size 10 cm^{-1} , but not when a spectral line appears between two consecutive grid points. In this case we inserted 12 points with a step size of 0.5 cm^{-1} into this

interval, which include the exact location of the center of the line.

For the infrared spectrum we used the intensities as given by the DFT-B3LYP/6-311+G** calculations and converted them to relative transmittance. The calculated vibrational Raman and infrared spectra of the three molecules are shown in Figs. 3, 4, 5, 6, 7 and 8.

Discussion

The chemistry and properties of organosulfones [14, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30] and *organoselenium* compounds [31, 32, 33, 34, 35, 36, 37] have attracted our attention to investigate the conformational and structural stability of vinyl sulfonyl halides [15] and their selenium derivatives in the present study. From the energy optimization it was clear that the *gauche* conformation is the lowest energy form for vinyl selenonyl fluoride, chloride

Table 6 Calculated vibrational frequencies (cm^{-1}) at B3LYP/6-311+G** level for the *gauche* conformer of vinyl selenonyl bromide^a

Sym	No.	Freq.	IR int.	Raman act.	Depol. ratio	PED
A	ν_1	3,231	3.8	89.9	0.5	90% CH ₂ antisym. str. (S ₂)
	ν_2	3,212	2.8	84.2	0.3	89% C–H str. (S ₁)
	ν_3	3,136	1.7	164.9	0.2	98% CH ₂ sym. str. (S ₃)
	ν_4	1,648	0.8	18.9	0.1	79% C=C str. (S ₇) 18% CH ₂ deformation (scissor) (S ₈)
	ν_5	1,405	18.4	24.3	0.3	82% CH ₂ deform. (scissor) (S ₈) 16% C=C str. (S ₇)
	ν_6	1,238	18.6	10.3	0.2	73% CH bend (S ₁₄) 22% CH ₂ wag (S ₉)
	ν_7	1,014	44.4	0.4	0.7	96% CH ₂ def. I (S ₁₉)
	ν_8	998	5.6	3.4	0.7	67% CH ₂ wag (S ₉) 23% CH bend (S ₁₄)
	ν_9	956	10.7	1.6	0.4	68% CH bend (S ₁₈) 20% CH ₂ def. II (S ₂₀)
	ν_{10}	947	92.6	16.8	0.7	97% SeO ₂ antisym. str. (S ₁₅)
	ν_{11}	879	73.1	33.3	0.1	99% SeO ₂ sym. str. (S ₄)
	ν_{12}	587	52.6	3.3	0.7	65% CH ₂ def. II (S ₂₀) 30% CH bend (S ₁₈)
	ν_{13}	562	8.9	11.2	0.1	72% C–Se str. (S ₅) 16% CCSe bend (S ₁₃)
	ν_{14}	378	33.8	3.3	0.4	38% CCSe bend (S ₁₃) 21% SeO ₂ rock (S ₁₀) 15% C–Se str. (S ₅) 12% SeO ₂ wag (S ₁₆)
	ν_{15}	327	56.8	2.5	0.5	78% SeO ₂ def. (scissor) (S ₁₁) 12% Se–Br str. (S ₆)
	ν_{16}	294	45.9	10.8	0.3	56% SeO ₂ rock (S ₁₀) 11% C–Se str. (S ₅)
	ν_{17}	216	3.1	20.1	0.35	78% Se–Br str. (S ₆) 15% SeO ₂ rock (S ₁₀)
	ν_{18}	193	3.8	2.2	0.6	63% SeO ₂ wag (S ₁₆) 15% SeO ₂ twist (S ₁₇)
	ν_{19}	179	0.1	3.6	0.6	76% SeO ₂ twist (S ₁₇) 17% CCSe bend (S ₁₃)
	ν_{20}	145	2.5	3.2	0.7	68% CSeBr bend (S ₁₂) 17% asym. torsion (S ₂₁)
	ν_{21}	79	0.4	6.9	0.7	77% asym. torsion (S ₂₁) 21% CSeCl bend (S ₁₂)

^a IR intensities and Raman activities are calculated in Km mol^{-1} and $\text{\AA}^4 \text{amu}^{-1}$, respectively

and bromide. It was interesting to notice that in the *gauche* conformation, the vinyl group was predicted to nearly eclipse one of the Se=O bonds with a torsional angle of about 100° (Table 1). This relative stability can be attributed to noticeable conjugation forces between the two groups that stabilized the *gauche* and not the *cis* or *trans* conformations in vinyl selenonyl halides.

The vibrational wavenumbers of vinyl selenonyl fluoride, chloride and bromide in the *gauche* conformation were calculated and vibrational infrared and Raman spectra were plotted in Figs. 3, 4, 5, 6, 7 and 8. The vibrational assignments of most of the fundamental vibrations of the three molecules were straightforward based on the calculated PED, particularly in the case of the chloride as shown in Table 5. Some of the calculated modes were predicted to mix significantly with other modes. The assignments of the normal modes that are associated with the vinyl $\text{H}_2\text{C}=\text{CH}-$ moiety in vinyl selenonyl fluoride (Table 4) and chloride (Table 5) were

compared with the corresponding reported ones for propenoyl fluoride and chloride. [6]

There are three stretches associated with the C–H moiety (S₁, S₂ and S₃) in vinyl selenonyl halides. These stretches were calculated to have the highest activities in the Raman spectra of vinyl selenonyl halides (Tables 4, 5 and 6). The two Se=O symmetric (S₄) and antisymmetric (S₁₅) stretching modes were calculated at 887 and 956 cm^{-1} and reveal a small degree of mixing for the chloride (Table 5). The assignment of this fundamental vibration was straightforward to the line with the second highest line intensity in the infrared spectra of the molecules (Tables 4, 5 and 6). The assignment of the corresponding ones for vinyl selenonyl fluoride was to the calculated wavenumbers at 905 and 976 cm^{-1} with high infrared intensities (Table 4). The C=C stretch was observed at 1,623 and $1,630 \text{ cm}^{-1}$ in the Raman spectra of propenoyl chloride and fluoride [6] in excellent agreement with those calculated at 1,649 and $1,652 \text{ cm}^{-1}$ for vinyl selenonyl chloride and fluoride, respectively.

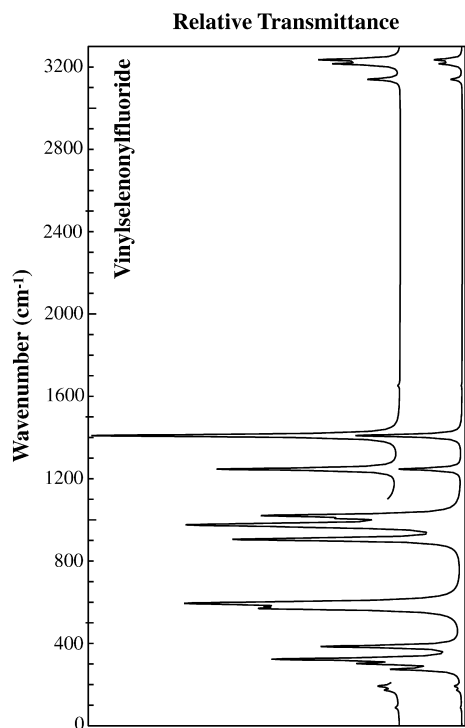


Fig. 3 Calculated vibrational infrared spectrum of vinyl selenonyl fluoride at the DFT-B3LYP/6-311+G** level

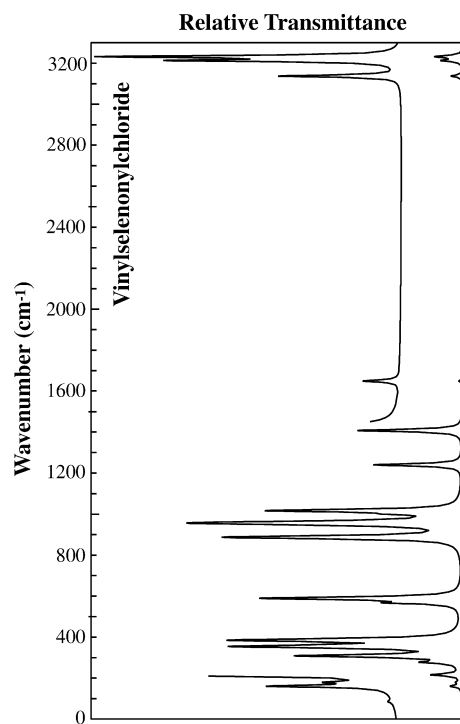


Fig. 5 Calculated vibrational infrared spectrum of vinyl selenonyl chloride at the DFT-B3LYP/6-311+G** level

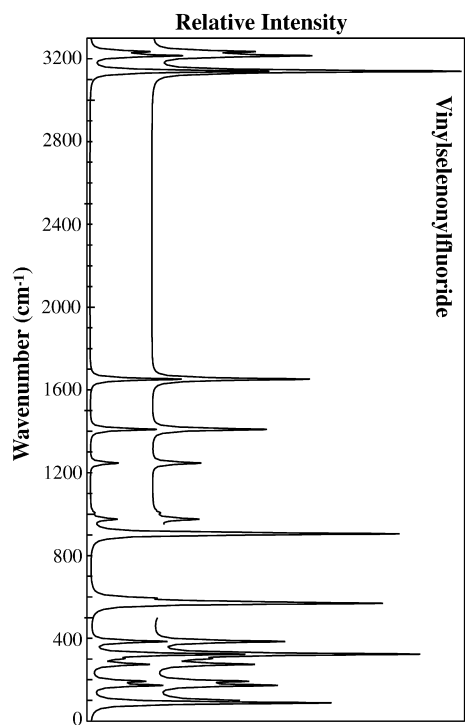


Fig. 4 Calculated vibrational Raman spectrum of vinyl selenonyl fluoride at the DFT-B3LYP/6-311+G** level

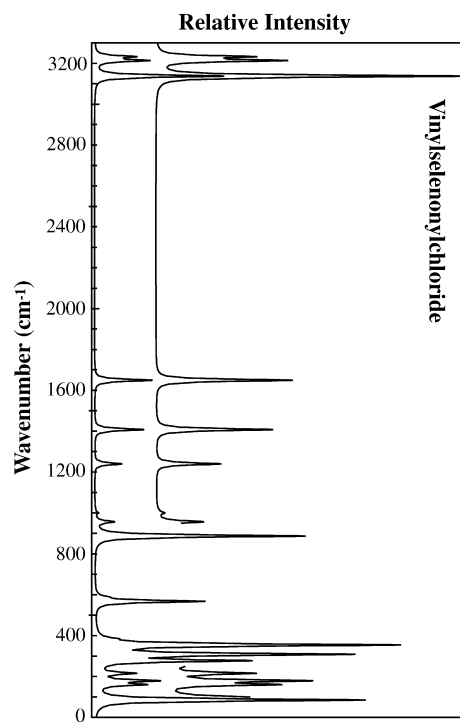


Fig. 6 Calculated vibrational Raman spectrum of vinyl selenonyl chloride at the DFT-B3LYP/6-311+G** level

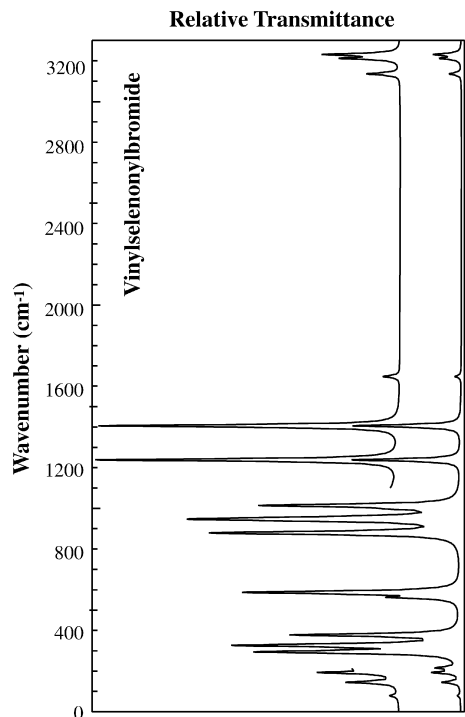


Fig. 7 Calculated vibrational infrared spectrum of vinyl selenonyl bromide at the DFT-B3LYP/6-311+G** level

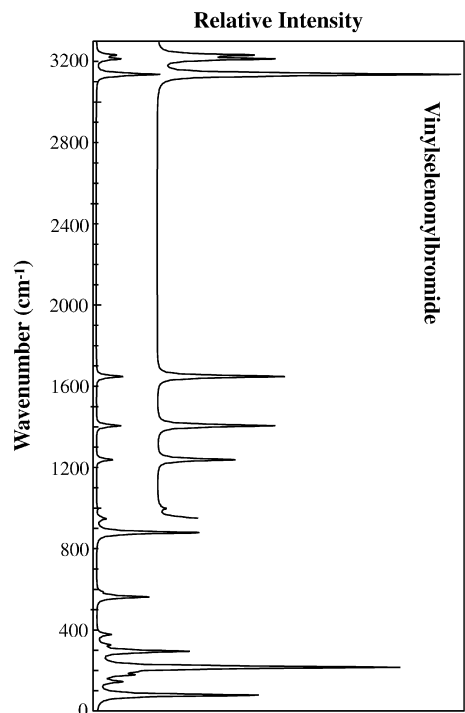


Fig. 8 Calculated vibrational Raman spectrum of vinyl selenonyl bromide at the DFT-B3LYP/6-311+G** level

The assignments of the C–Se and Se–F stretching modes in the spectra of vinyl selenonyl fluoride were made directly to the calculated wavenumbers at 579 cm^{-1} (55% PED) and 569 cm^{-1} (62% PED), as shown in Table 4. The corresponding C–Se and Se–Cl modes were calculated in the spectra of the chloride at 568 cm^{-1} (71% PED) and 354 cm^{-1} (50% PED), respectively with relatively high infrared intensities, as shown in Table 5. For the bromide these two modes were calculated at 562 cm^{-1} (72% PED) and 216 cm^{-1} (78% PED), as shown in Table 6.

The two CH bending modes (S_{14} and S_{18}) in the fluoride and the chloride were calculated in reasonable agreement with those observed for propenoyl fluoride and chloride. [6] The S_{14} modes were calculated at $1,246$ and $1,240\text{ cm}^{-1}$ in the spectra of vinyl selenonyl fluoride and chloride that are consistent with the observed ones at $1,298$ and $1,279\text{ cm}^{-1}$ in the infrared spectra of the gaseous propenoyl fluoride and chloride, respectively. On the other hand, the S_{18} modes were calculated to be a little higher than those observed of the propenoyl halides. The assignments of the four CH_2 -bending modes in each of the three molecules (S_8 , S_9 , S_{19} and S_{20}) were straightforward based on their calculated PED values. For example, in the spectrum of vinyl selenonyl chloride these modes were calculated at $1,408\text{ cm}^{-1}$ (82%), $1,001\text{ cm}^{-1}$ (62%), $1,017\text{ cm}^{-1}$ (97%) and 589 cm^{-1} (61%) respectively.

Some of the four bending modes associated with the SeO_2 group in the three molecules were calculated to have a high degree of mixing with other vibrations as shown in Tables 4, 5 and 6. The same thing was noticed with the CCSe bending mode (Tables 4, 5 and 6). However, the CSeF (77% PED), the CSeCl (81% PED) and CSeBr (77% PED) could be assigned to the wavenumbers calculated at 193 , 161 , 145 cm^{-1} in the spectra of the fluoride, chloride and the bromide, respectively. Finally, the lowest calculated wavenumbers in the spectra of the three molecules were the asymmetric torsions with a negligible degree of mixing.

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