Structural Stability and Vibrational Analyses of Haloselenonyl Azides, XSeO$_2$-NNN, where X is F, Cl, Br

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Abstract: The structural stability of haloselenonyl azides was investigated by quantum mechanical Møller-Plesset perturbation theory of second order and density functional theory calculations. The 6-311+G** basis set was used to include polarization and diffuse functions in the calculations at the DFT-B3LYP level. The potential scans for the rotation of the -NNN rotor were calculated and found to be consistent with a single minimum that corresponds to a *gauche* conformation (-NNN moiety nearly eclipses one of the two selenonyl Se=O bonds) for the three halogens at ambient temperature. The structural parameters for the minima calculated by MP2 and DFT turned out to be very similar. The vibrational modes, infrared and Raman intensities as well as depolarization ratios were calculated at DFT-B3LYP/6-311+G** level for the three molecules in their *gauche* conformations. The potential energy distributions among symmetry coordinates of the normal modes of the molecules in their *gauche* conformation were then computed from normal coordinate analyses.

Introduction

The conformational behavior of fluorosulfonyl isocyanate F-SO$_2$-NCO and chlorosulfonyl isocyanate Cl-SO$_2$-NCO has drawn the attention of structural chemists and spectroscopists because of their interesting structure and importance in chemistry [1-6]. They have been investigated over the past few years by both theoretical and spectroscopic methods. Chlorosulfonyl isocyanate in particular has been used extensively as chemical precursor in many (2+2)-cycloaddition reactions [7-10] and in drug synthesis [11-12].

From an electron diffraction study, the conformational stability of chlorosulfonyl isocyanate was characterized in two ways [1]. First, the compound was described as a mixture of two forms having Cl-S-N=C rotational angles of 109° and 70°, respectively, in which the first form predominates (69%). Second, the substance was described as one form having a rotation angle of 86° and a large amplitude of rotation around the S-N bond [1]. Microwave studies on the same molecule indicated that the Cl-S-N=C dihedral angle is 94° and that the NCO group is not linear for the lowest energy conformer [2]. A later *ab initio* study predicted a single *gauche* conformation with a Cl-S-N=C dihedral angle of 104.8° [3].

Additionally, the IR and Raman spectra of the liquid and vapor phases of chlorosulfonyl isocyanate were reported and all data were interpreted based on a single *gauche* conformer in both phases [4]. In a more complete investigation of the IR spectrum of the compound dissolved in liquid Xenon as a function of temperature it was determined that a single *gauche* conformer is present in all phases [6]. Similarly, fluorosulfonyl isocyanate was determined to exist as a single *gauche* conformation with an FSNC dihedral angle of about 108° where again the NCO group nearly eclipses one S=O bond [5].

In a previous study [13], we investigated the structural stability of the corresponding azides X-SO$_2$-NNN (X is fluoride and chloride) for the purpose of comparison. We calculated the potential function scans for fluoro- and chlorosulfonyl azides at the density functional B3LYP/6-311++G** level of calculation. In addition, vibrational modes were calculated and normal coordinate calculations were carried out to compute the potential energy distributions (PED) among symmetry coordinates of all normal modes for the two molecules in their stable *gauche* conformation. The assignments of the vibrational modes were made based on calculated PED values and experimental data reported for similar molecules [5,6].

Since selenium compounds are very important in synthesis and also in medical applications [14-20], we give in the present study the properties of the corresponding selenium compounds (X-SeO$_2$-NNN, X = F, Cl and Br). Especially we were interested in the question, whether or not the selenium atom, being larger than sulfur, could change the geometry such that conjugation between the Se=O and the N=N bonds might be reduced, which would in turn reduce the preference of the *gauche* conformation over others. Further we provide a reliable assignment of the vibrational modes in the spectra of the compounds in order to facilitate future spectroscopic studies of these materials.

The very high reactivity and the application of organoazides in synthetic chemistry and many important industries [21-36] has drawn the attention to investigate the structure and conformational behavior of vinyl azide, CH$_2$=CH-NNN [37] and formyl azide, CHO-NNN [38], by DFT and ab initio MP2 calculations. Both molecules were predicted to have a *cis/trans* conformational equilibrium with the *gauche* form being the transition state. The stability of both molecules in only the planar forms was attributed to the following conjugated resonance structures:

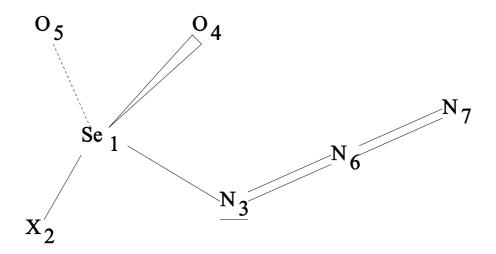$$R\text{-}N^-\text{-}N^+ \equiv N \ <=> \ R\text{-}N=N^+=N^-$$

where *R* is a vinyl, CH$_2$=CH-, or a formyl, -CH=O, group. This turned our attention to investigate another interesting series, halosulfonyl azides XSO$_2$-NNN (X is F and Cl) in a previous work [13]. From energy optimizations and calculated potential scans fluoro- and chlorosulfonyl azides were predicted to exist only as the *gauche* conformation similar to the corresponding isocyanates XSO$_2$-NCO [1-6]. An identical result we find in the present study on haloselenonyl azides with X being F, Cl and Br. Thus the larger Se atom, in comparison to S, does not change the geometries to an extent that would make the resonance between one

of the Se=O and the N=N double bonds less effective in determining the equilibrium to be the *gauche* structure. From full optimization the *gauche* conformation of haloselenonyl azides is predicted to have a torsional angle of about 80° in which the -NNN moiety nearly eclipses one of the two selenonyl Se=O bonds. In such a configuration the *gauche* conformation is most probably stabilized through conjugation effects in a similar way as in formyl and vinyl azides [37,38]. The two N-N bonds of the azide groups are calculated to be of a length of about 1.25 and 1.13 Å, consistent with double and triple bond characters. This supports the nature of the above conjugated resonance structure of the azide moiety in haloselenonyl azides as well as in formyl and vinyl azides [37,38].

Ab initio calculations

The GAUSSIAN 98 program [39], running on an IBM RS/6000 43P model 260 workstation, was used to carry out the DFT/B3LYP and MP2 calculations. The 6-311+G** basis set was employed to optimize the structures and predict the energies, structural parameters, dipole moments, and rotational constants of fluoro-, chloro- and bromoselenonyl azides in their possible stable structures. The geometry and atom numbering is shown in Figure 1; the results are shown in Table 1. It should be noted that since differences between the MP2 and DFT results are not pronounced, we could use the faster DFT method for all further calculations.

Figure 1: Atom numbering for haloselenonyl azides (X is F, Cl and Br).
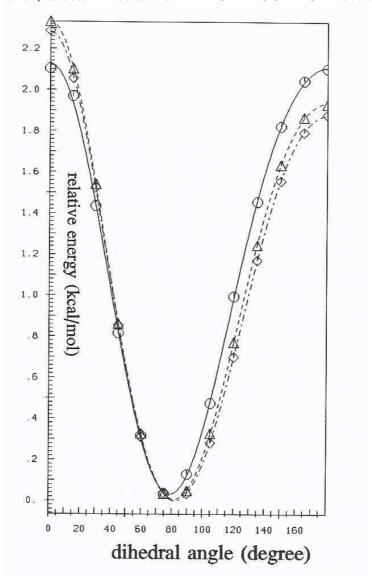

X = F, Cl and Br

Torsional potential scans

The potential scans for the internal rotation about the N-Se single bonds were obtained by allowing the

XSeNN dihedral angles (Φ) in the molecules to vary from 0° (cis position) to 180° (trans position). Full geometry optimizations at each of the fixed dihedral angles $\Phi = 15^o$, 30°, 45°, 60°, 75°, 90°, 105°, 120°, 135°, 150°, and 165° were carried out at the DFT level of calculation. The potential function scans in the three molecules are shown in Figure 2. Each one of the three potential curves is consistent with one minimum that corresponds to the *gauche* (Φ about 80°) conformation as shown in Figure 2. The optimized structural parameters (calculated both with MP2 and DFT) and energies of the molecules in the *gauche* conformation are listed in Table 1.

Figure 2: Potential curves for the torsional potentials in fluoroselenonyl azide (solid line, DFT points as hexagons), in chloroselenonyl azide (dashed line, DFT points as triangles) and in bromoselenonyl azide (dashed dotted line, DFT points as diamonds) as determined at the DFT-B3LYP/6-311+G** level.

Table 1: Structural parameters, total dipole moments and rotational constants for the *gauche* conformer of haloselenonyl azides (X = F, Cl and Br), calculated on MP2 and DFT levels, using the 6-311+G** basis set.

MP2			
Parameter	X = F	X = Cl	X = Br
bond lengths (Å)			
$Se_1 - X_2$	1.7747	2.1874	2.3572
$Se_1 - N_3$	1.8391	1.8599	1.8688
$Se_1 = O_4$	1.5941	1.5994	1.6018
$Se_1 = O_5$	1.5847	1.5903	1.5930
$N_3 = N_6$	1.2568	1.2542	1.2532
$N_6 = N_7$	1.1501	1.1518	1.1525
bond angles (degree)			
$(N_3Se_1X_2)$	96.65	99.08	99.70
$(X_2Se_1O_4)$	104.72	106.43	107.12
$(X_2Se_1O_5)$	106.33	107.83	108.54
$(Se_1N_3N_6)$	111.41	110.92	110.87
$(N_3N_6N_7)$	171.97	172.42	172.83
torsional angles (degree)			
$(N_3X_2Se_1O_4)$	113.60	113.41	113.41
$(N_3X_2Se_1O_5)$	-108.84	-108.71	-108.67
$(X_2Se_1N_3N_6)$	76.18	76.18	73.87
total energy (H)			
E_t	-2813.4541988	-3173.4367477	-5286.2910420
total dipole moment (Debye)			
μ_t	3.2588	3.2584	3.4999
rotational constants (GHz)			
A	3.85980	2.30429	1.61847
B	1.47242	1.42066	1.14392
C	1.46064	1.14140	0.81268
DFT/B3LYP			
Parameter	X = F	X = Cl	X = Br
bond lengths (Å)			
$Se_1 - X_2$	1.7869	2.2231	2.3866
$Se_1 - N_3$	1.8757	1.9001	1.9088
$Se_1 = O_4$	1.6082	1.6148	1.6176
$Se_1 = O_5$	1.5990	1.6057	1.6086
$N_3 = N_6$	1.2519	1.2480	1.2466
$N_6 = N_7$	1.1248	1.1267	1.1274
bond angles (degrees)			
$(N_3Se_1X_2)$	97.13	100.30	101.22
$(X_2Se_1O_4)$	105.03	106.97	107.70
$(X_2Se_1O_5)$	106.44	107.72	108.25
$(Se_1N_3N_6)$	112.34	112.15	112.16
$(N_3N_6N_7)$	172.45	173.36	173.50

Table 1. Cont.

torsional angles (degrees)			
$(N_3X_2Se_1O_4)$	114.35	114.23	114.18
$(N_3X_2Se_1O_5)$	-108.91	-109.12	-109.18
$(X_2Se_1N_3N_6)$	79.03	82.75	84.06
total energy (H)			
E_t	-2816.0122882	-3176.376035	-5290.3039151
total dipole moment (Debye)			
μ_t	2.2964	2.1935	2.3910
rotational constants (GHz)			
A	3.77760	2. 28284	1.70586
B	1.44238	1.35332	1.02641
C	1.42986	1.09894	0.77273

Obviously there is not much difference between the structural parameters, calculated with the help of the MP2 or the DFT method. Thus all further numbers and plots given are calculated on DFT level. Interestingly, dipole moments and rotational constants show a larger difference between their MP2 and DFT values, however, they are still comparable. The potential curves were fitted in a Fourier cosine series of the form

$$E = E_o + \sum_{k=0}^{6} \frac{V_k}{2}(1 + \delta_{k0})\left[1 - (1 - \delta_{k0})\cos(k\phi)\right]$$

where E_o is the total energy in the absolute energy minimum, to which the potential refers, and V_o is the energy difference between the *cis* form and the absolute minimum of the energy. The potential constants for the three molecules are given in Table 2.

Table 2: Calculated potential constants in kcal/mol (see equation in the text) for the torsional potentials in the three haloselenonyl azides (X = F, Cl and Br) together with the root mean square deviations, rms in kcal/mol, for the fits, as well as E_0 in Hartree to which the relative energies refer (all on DFT/B3LYP level).

Quantity	X = F	X = Cl	X = Br
V_0	2.0910	2.2961	2.2462
V_1	0.4423	0.7409×10^{-1}	0.1828×10^{-1}
V_2	-1.9892	-2.0817	-2.0485
V_3	-0.4604	-0.4314	-0.3915
V_4	0.2529×10^{-1}	-0.3348×10^{-1}	-0.4481×10^{-1}
V_5	0.7158×10^{-3}	-0.3756×10^{-1}	-0.3175×10^{-1}
V_6	-0.5353×10^{-2}	-0.1161×10^{-2}	0.5389×10^{-2}
rms	0.1368×10^{-1}	0.3625×10^{-2}	0.4879×10^{-2}
E_0	-2816.012294	-3176.376037	-5290.303921

The potential curves for the three different halogen substituted molecules are very similar, far more than in case of a sulfur atom [13] instead of selenium. Probably in case of the larger Se atom, the differences between the halogens show effects which are less pronounced than for the smaller S atom.

Vibrational modes and normal coordinate analyses

The optimized structural parameters were used to compute the vibrational modes of the three halo-selenonyl azide molecules at the DFT-B3LYP/6-311+G** level. The three molecules in their *gauche* conformations have C_1 symmetry where the 15 vibrational modes span the irreducible representation 15 A and should be polarized in the Raman spectra of the liquids. Normal coordinate analyses were carried out for the molecules in their *gauche* conformations as described previously [40, 41]. The internal and symmetry coordinates of the molecules are listed in Tables 3 and 4. Note that the set of internal coordinates is over-complete to make the construction of symmetry coordinates easier. Redundant internal coordinates are removed by the program automatically.

Table 3: Over-complete set of internal coordinate definitions for haloselenonyl azides (X = F, Cl or Br; for atom denotation see Figure 1)

No.	Coordinate	Definition	
1	Se_1-X_2	stretch	Q
2	Se_1-N_3	stretch	T
3	Se_1-O_4	stretch	X_1
4	Se_1-O_5	stretch	X_2
5	N_3-N_6	stretch	R_1
6	N_6-N_7	stretch	R_2
7	$N_3Se_1X_2$	bend	θ
8	$X_2Se_1O_4$	bend	ε_1
9	$X_2Se_1O_5$	bend	ε_2
10	$O_4Se_1O_3$	bend	π_1
11	$O_5Se_1O_3$	bend	π_2
12	$O_4Se_1O_5$	bend	δ
13	$Se_1N_3N_6$	bend	γ
14	$N_3N_6N_7$	bend	σ_1
15	$N_7N_6N_3Se_1$	wag	σ_2
16	$N_6N_3Se_1O_4 + N_6N_3Se_1O_5$	torsion	τ

The potential energy distributions (PED) among the symmetry coordinates for each of the normal modes of the molecules were calculated at DFT/B3LYP level and listed in Table 5. A complete assignment of the fundamentals was proposed based on the calculated PED values, infrared band intensities, Raman line activities, and depolarization ratios. The data of the assignments of the vibrational modes are also listed in Table 5.

Table 4: Symmetry coordinate definitions (all of them are of species A) for *gauche* halo-selenonyl azides (not normalized).

Description	Symmetry coordinate
X - Se stretch	$S_1 = Q$
Se - N stretch	$S_2 = T$
NNN symmetric stretch	$S_3 = R_1 + R_2$
SeO$_2$ symmetric stretch	$S_4 = X_1 + X_2$
NNN antisymmetric stretch	$S_5 = R_1 - R_2$
SeO$_2$ antisymmetric stretch	$S_6 = X_1 - X_2$
XSeN bend	$S_7 = 5\theta - \varepsilon_1 - \varepsilon_2 - \pi_1 - \pi_2 - \delta$
SeNN bend	$S_8 = \gamma$
NNN in-plane bend	$S_9 = \sigma_1$
NNN out-of-plane bend	$S_{10} = \sigma_2$
SeO$_2$ deformation	$S_{11} = 4\delta - \varepsilon_1 - \varepsilon_2 - \pi_1 - \pi_2$
SeO$_2$ rock	$S_{12} = \varepsilon_1 - \varepsilon_2 + \pi_1 - \pi_2$
SeO$_2$ twist	$S_{13} = \varepsilon_1 - \varepsilon_2 - \pi_1 + \pi_2$
SeO$_2$ wag	$S_{14} = \varepsilon_1 + \varepsilon_2 - \pi_1 - \pi_2$
NNN torsion	$S_{15} = \tau$

Table 5: DFT wavenumbers, k_i in cm^{-1} (all symmetry species are A), infrared intensities, I_i in km mol^{-1}, Raman activities, S_i in Å^4 amu^{-1}, depolarization ratios ρ_i and distribution of the potential energy of a normal mode in the symmetry coordinates, PED (only values larger than 10% are given), for the normal modes i in halo-selenonylazides.
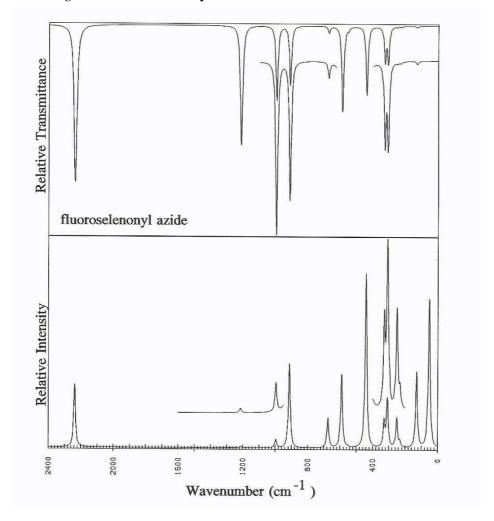
k_i	I_i	S_i	ρ_i	PED
			Fluoroselenonyl azide (X = F)	
2237	411.8	133.6	0.36	88% S_5, 12% S_3
1214	206.6	3.4	0.72	85% S_3, 13% S_5
996	99.7	12.7	0.64	98% S_6
912	75.2	28.7	0.07	97% S_4
675	7.1	9.1	0.20	49% S_9, 31% S_8, 17% S_2
591	120.4	15.1	0.09	97% S_1
554	3.1	0.9	0.67	96% S_{10}
441	90.1	25.8	0.12	68% S_2, 17% S_9
329	40.2	5.0	0.44	30% S_{12}, 22% S_{11}, 18% S_{14}, 13% S_9
311	22.2	6.0	0.62	70% S_{14}, 15% S_{12}
308	21.7	6.7	0.53	47% S_{11}, 35% S_{12}
251	0.8	6.4	0.62	78% S_{13}
231	0.7	1.6	0.74	78% S_7, 17% S_{11}
130	1.4	4.0	0.52	54% S_8, 15% S_{12}, 15% S_{13}, 14% S_9
52	0.0	3.3	0.75	95% S_{15}

Table 5. Cont.

Chloroselenonyl azide (X = Cl)				
2221	444.1	154.9	0.37	88% S_5, 12% S_3
1220	201.1	4.5	0.75	86% S_3, 13% S_5
977	92.6	15.9	0.64	97% S_6
899	77.2	30.2	0.05	97% S_4
669	4.8	9.5	0.19	51% S_9, 32% S_8, 14% S_2
550	4.8	0.9	0.63	97% S_{10}
420	86.6	29.7	0.15	72% S_2, 16% S_9
378	123.1	15.6	0.11	67% S_1, 17% S_{14}, 12% S_{11}
311	29.6	6.1	0.36	42% S_{11}, 24% S_{14}, 11% S_{12}
289	5.3	18.6	0.36	43% S_{14}, 32% S_1, 22% S_{11}
281	4.8	10.6	0.53	47% S_{12}, 11% S_{11}
211	1.2	4.8	0.70	76% S_{13}, 18% S_{12}
188	1.4	2.8	0.75	83% S_7
126	1.2	5.2	0.47	53% S_8, 17% S_{12}, 14% S_9, 11% S_{13}
38	0.1	6.6	0.74	95% S_{15}
Bromoselenonyl azide (X = Br)				
2215	458.4	167.5	0.37	88% S_5, 12% S_3
1223	199.7	5.3	0.75	86% S_3, 13% S_5
970	90.6	18.5	0.65	97% S_6
893	78.5	31.9	0.05	97% S_4
668	4.6	9.4	0.20	52% S_9, 32% S_8, 13% S_2
550	4.4	1.0	0.56	97% S_{10}
412	85.2	34.0	0.16	74% S_2, 15% S_9
341	109.8	2.5	0.21	40% S_{14}, 32% S_{11}, 20% S_1
306	27.1	5.5	0.36	39% S_{11}, 30 S_{14}
275	3.3	1.7	0.49	42% S_{12}, 13% S_{13}, 11% S_{11}
222	1.1	23.1	0.25	78% S_1, 15% S_{14}
188	1.0	2.9	0.71	70% S_{13}, 21% S_{12}
165	1.6	2.6	0.74	75% S_7
123	1.2	5.5	0.43	50% S_8, 16% S_{12}, 14% S_7, 13% S_9
33	0.1	7.2	0.73	94% S_{15}

The vibrational infrared and Raman spectra were calculated using the computational methods previously described [41,42]. To calculate the Raman spectra, the wavenumbers k_j, the scattering activities S_j, and the depolarization ratios ρ_i were obtained from the DFT-B3LYP calculations. The calculated vibrational Raman and infrared spectra of the molecules in the *gauche* conformations at DFT level are shown in Figures 3-5.

Figure 3:   Calculated vibrational infrared (upper panel) and Raman (lower panel) spectra for the *gauche* fluoroselenonyl azide at the DFT-B3LYP/6-311+G** level.
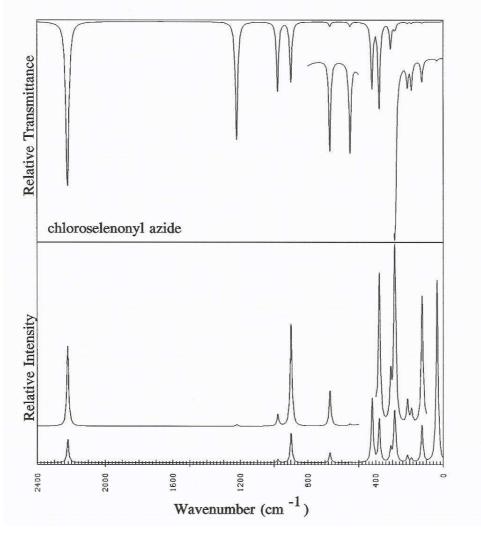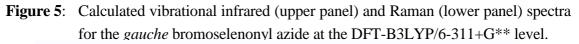

Discussion

We calculated the vibrational modes of the three molecules in their *gauche* conformation and plotted their vibrational infrared and Raman spectra as shown in Figures 3-5. The vibrational assignments of most of the fundamental vibrations of the three molecules were straightforwardly based on the calculated PED as shown in Table 5.
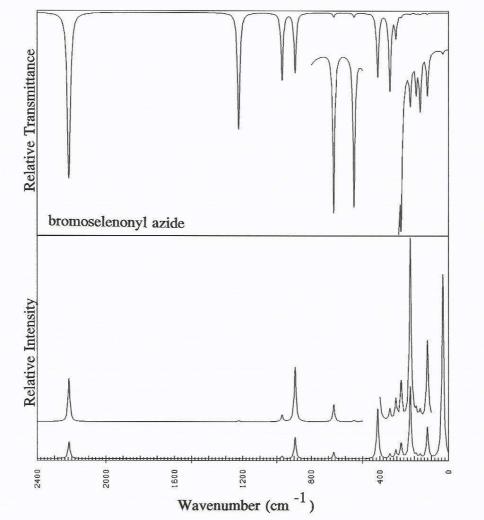
Besides differences in relative intensities, the five bands with the highest wavenumbers in the spectra of all three molecules are very similar. The highest band is mainly NNN symmetric stretch (about 90%) between 2215 and 2237 cm^{-1}, the next lower one is predominantly NNN antisymmetric stretch (about 90%) between 1214 and 1223 cm^{-1}. Both, wavenumbers and assignments are similar to the corresponding sulfonyl compounds [13]. The following two bands are SeO$_2$ antisymmetric stretch (97-98% PED) between 970 and 996 cm^{-1} and SeO$_2$ symmetric stretch (97% PED) between 893 and 912 cm^{-1}. The modes are considerably lower than those found in the sulfonyl compounds, where they appear at about 1200 and 1400 cm^{-1}. This is probably due to the fact that the Se atom is heavier than the S atom. The following band between 668 and 675 cm^{-1} is higly mixed in the three halogenated molecules, consisting of 49 - 52% NNN in-plane bend, 31-32% SeNN bend and of 13-17% Se - N stretch at 668 - 675 cm^{-1}.

Figure 4: Calculated vibrational infrared (upper panel) and Raman (lower panel) spectra
for the *gauche* chloroselenonyl azide at the DFT-B3LYP/6-311+G** level.

In fluoroselenonyl azide the next band is nearly pure (97% PED) F-Se stretch at 591 cm^{-1}. For the other molecules the X-Se stretch appears lower in wavenumber and is highly mixed with other motions, corresponding to the expectation that the F-Se bond should be stronger than the Cl-Se bond, which is stronger than the Br-Se bond. In the chlorinated molecule Cl-Se stretch appears with 67% PED at 378 cm^{-1}, mixed with 17% SeO$_2$ wag and 12% SeO$_2$ deformation. In the bromo derivative the Br-Se stretch appears with 78% PED at 222 cm^{-1}, mixed with 15% SeO$_2$ wag, while the deformation contribution here is less than 10%. However, in the bromo derivative there is a second band that contains Br-Se contributions (20% PED) at 341 cm^{-1} that probably corresponds more to the two other ones in the fluoro and chloro derivatives discussed above, because the former band has an IR intensity of only 1.1 km mol^{-1}, while the latter one has 109.8 km mol^{-1}, comparing better with 120.4 km mol^{-1} in the fluoro compound and 123.1 km mol^{-1} in the chlorinated molecule. One would have expected that the infrared intensities should decrease when going from F to Cl and on to Br, because of the decreasing dipole moments of the bonds. However, note that the Se-F stretch is a pure vibration, while Se-Cl and Se-Br stretches appear to be highly mixed, making the argument less clear. The same is important for the corresponding Raman intensities which should increase because of the increasing polarizabilities of Se-F, Se-Cl and Se-Br bonds. Note, that such IR intensities actually are integrated absorption coefficients and thus proportional to the peak absorbance of an IR line given a Lorentzian shape.

Figure 5: Calculated vibrational infrared (upper panel) and Raman (lower panel) spectra
for the *gauche* bromoselenonyl azide at the DFT-B3LYP/6-311+G** level.

Next we have a band between 550 and 554 cm^{-1} which is pure NNN out-of-plane bend in all the three
compounds. Following is a mixture of 68-74% Se-N stretch with 15-17% NNN in-plane bend at 412 to 441
cm^{-1}. The S-N stretch in isocyanates in contrast is found around 760 cm^{-1} [4,5] while it was calculated at
around 720 cm^{-1} in the halosulfonyl azides [13]. The following modes in the three spectra are all highly
mixed, consisting mostly of SeO_2 motions, and appear between 300 and 400 cm^{-1}. X-Se-N bend is between
165 cm^{-1} and 231 cm^{-1} with different degrees of mixing. The lowest band is in all three cases nearly pure
(about 95% PED) NNN torsion between 33 and 52 cm^{-1} and has high Raman intensities and negligible
transmittances in the IR spectra.

Acknowledgements

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