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Gas-Phase Infrared Spectra of Vinyl Selenol and Vinyl Tellurol

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The infrared spectra (3500−500 cm^{-1}) of gaseous vinyl selenol and vinyl tellurol have been recorded at 0.1 cm^{-1} resolution. For the latter the spectra were obtained at room temperature, but for the former a temperature of −40 °C was required because of the chemical instability of vinyl selenol at room temperature. To compensate the very weak vapor pressure of vinyl tellurol at room temperature, a long optical path up to 136 m was necessary to record its spectrum. B3LYP density functional theory (DFT) calculations have been performed to assign the different absorption bands. Since an unambiguous assignment of the absorption bands requires a precise knowledge on the relative abundance of the syn and gauche rotamers of these compounds, their relative energies and their anharmonic vibrational frequencies were obtained using a very extended Def2-QZVP basis set. Two rotamers, the syn, which is planar, and a nonplanar gauche, were found to be local minima for both compounds. The gauche rotamer presents two degenerate conformers, which differ by the position of the SeH (TeH) hydrogen atom above or below the molecular plane. Our theoretical results are in good agreement with the main features of the experimental spectra. Fundamental bands and some combination bands of vinyl selenol and vinyl tellurol were assigned and compared with those of vinyl alcohol and vinyl thiol, whose spectra had been reported previously in the literature.

Introduction

The number of isolated primary vinylic heterocompounds remains mainly limited to the derivatives containing one of the first heteroatoms of columns 15 and 16 of the Periodic Table or one heteroatom of column 14. The silicon, germanium, tin, nitrogen, phosphorus, oxygen, and sulfur derivatives have thus been synthesized a long time ago.[1−3] Such primary α,β-unsaturated heterocompounds present a particular interest by the determination of the interaction between the unsaturated and the heteroatomic groups. In the case of oxygen and nitrogen derivatives, the consequence of these interactions is the tautomerism between the keto−enol and imine−enamine forms, respectively. For phosphorus or sulfur derivatives, rearrangements have been evidenced by the trapping of the intermediates with nucleophiles.[4,5] In the middle of the 1990′s, arsenic and antimony derivatives were added to the list.[6] Vinylic compounds $H_2C{=}CHX$ containing heteroatoms of column 15 of the Periodic Table have been quite recently studied in our groups. Structural and vibrational study of the two syn and gauche conformers of the vinyl phosphine $X = PH_2$,[7,8] vinyl arsine $X = AsH_2$,[9] and vinyl stibine $X = SbH_2$[9] and their heteroatom-dideuterated isotopomers have been investigated.

It was only in 2000 that the preparation of vinyl selenols and vinyl tellurols has been reported.[10] The main difficulties for the preparation of these compounds were to find a way compatible with the highly acidic character of the hydrogen on the heteroatom and their kinetic instability, an intrinsic property of any tellurol and of most of the primary vinylic heterocompounds including vinyl alcohol and vinyl thiol.

The infrared study concerning vinyl compounds, $H_2C{=}CH{-}XH$, with heteroatom (O, S, Se and Te) started with the study of the vinyl alcohol. This compound was identified by Hawkins and Andrews[11] among the products of reaction of atomic oxygen with ethylene in solid argon after UV irradiation. Rodeler et al.[12] reported the infrared spectra of matrix isolated vinyl alcohol generated by the pyrolysis of cyclobutanol. The first spectroscopic evidence of vinyl alcohol in the gas phase was published by Saito[13] in 1976, and 15 years later, the first gas-phase infrared spectrum was reported by Koga et al.[14] with the observation and assignment of 10 of the 15 fundamental bands. For the second vinyl derivative, the vinyl thiol, few data issued from spectra recorded in the gas phase were reported. Almond et al.[15] published the first preliminary report of the infrared spectrum of vinyl thiol in 1977, follow up by a detailed study of the vibrational gas-phase spectrum of this compound in 1983.[16] Both the syn and anti conformers considered as planar were assigned.

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The aims of this work are to extend these spectroscopic analyses to the next vinyl compounds of this series, namely, vinyl selenol (ethene selenol) and vinyl tellurol (ethene tellurol). The infrared spectra were recorded to detect both the syn and the gauche conformers predicted to be almost degenerate in energy, and the observed gas-phase vibrational bands in the range 3500−500 cm^{-1} have been analyzed. The comparisons of several vibrations bands of fundamental modes between molecules of the same vinyl series were made when data were available. The experimental study has been coupled with *ab initio* and density functional theory calculations, which greatly helped the rationalization of the spectra.

Experimental Section

Caution. *Vinyl selenol and vinyl tellurol are potentially highly toxic compounds and must be used with great care under a well-ventilated hood.*

The synthesis of vinyl selenol has already been reported.[10,17] Two approaches have been used to prepare a sample: the reaction of tributylstannane on divinyl diselenide[10] and the reaction of vinyl selenocyanide on dichloroalane followed by an acidification of the formed salt with succinic acid.[17] The vinyl tellurol was prepared as previously reported[10,18] starting from divinyl ditelluride.

Spectroscopic Section. The spectra discussed in this paper have been recorded with 0.1 cm^{-1} resolution between 500 and 3500 cm^{-1} using a globar source, KBr beam splitter and liquid nitrogen cooled MCT detector, in a Bruker HR120 FTIR spectrometer. For the detailed analysis of the infrared spectrum of vinyl selenol, a 30 cm White-type cell was used with 10 m optical path and typical pressure of 1−1.5 torr. It is difficult to obtain the vinyl selenol with a purity good enough for the spectroscopic analysis because of its kinetic instability in the gas phase at room temperature and the presence of byproduct. To reduce these unwanted effects, the gas cell was cooled down to −40 °C, but even under these conditions we observed the presence of traces of hydrogen cyanide (HCN) in the recorded spectrum. Fortunately, the infrared absorption bands of this byproduct are well-known, which allowed us to withdraw them from the analyzed vinyl selenol spectrum. Vinyl tellurol is rather stable and can be kept several hours, at room temperature, in the gas phase. On the other hand, its vapor pressure is extremely weak, less than 0.02 torr. In order to compensate for this factor, the use of a much longer optical path was necessary to record the spectrum. For this purpose, we used a gas cell with a base path length of 2 m, equipped with the White optical system which was adjusted to obtain an optical path up to 136 m. Recorded spectra are given in Figure 2.

Computational Details. The geometries of vinyl selenol and vinyl tellurol were optimized using the hybrid density functional B3LYP method, which combines the Becke's three-parameter nonlocal hybrid exchange potential[19] with the nonlocal correlation functional of Lee, Yang, and Parr.[20] This approach is known to provide reliable geometries and harmonic vibrational frequencies for a wide variety of systems.[21−25] The harmonic vibrational frequencies were evaluated employing the same method in order to verify that the stationary points found were local minima of the potential energy surface. Since we were interested in the interpretation of the corresponding infrared spectra, the anharmonic vibrational frequencies were also evaluated by numerical differentiation along modes as implemented in the Gaussian 03 suite of programs.[26] For this purpose a 6-311+G(3df,2p) basis set expansion was initially used. In order to get very reliable geometries and anharmonic vibrational frequencies, these geometries were further refined by using a much extended Def2-QZVP basis set,[27] and the anharmonic vibrational frequencies were reevaluated. For selenium, the Def2-QZVP is a very extended all-electron [24s, 20p, 10d, 4f,1 g/11s, 7p, 4d, 4f, 1g] basis set which includes 4f and 1g orbitals as polarization functions. For tellurium, this basis set includes a relativistic pseudopotential, which accounts for the main relativistic effects and a [17s, 14p, 11d, 4f,1 g/7s, 6p, 4d, 4f, 1g] basis expansion. For carbon and hydrogen, the Def2-QZVP basis set corresponds to the [15s, 8p, 3d, 4f,1 g/7s, 4p, 3d, 2f, 1g] and [7s, 3p, 2d, 1f/4s, 3p, 2d, 1f] expansions, respectively.

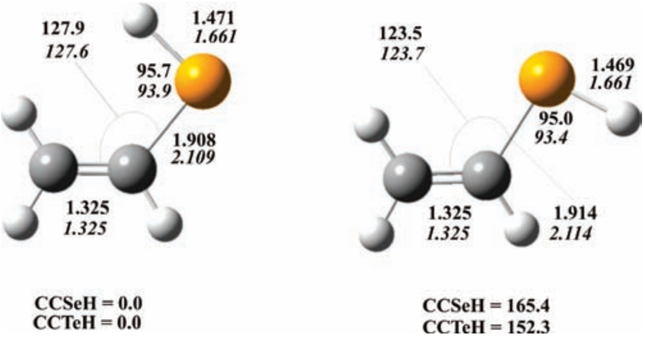

Figure 1. B3LYP/Def2-QZVP optimized structures of the two stable syn and gauche rotamers of the vinyl selenol and vinyl tellurol. Bond lengths are in angstroms and bond angles and dihedral angles in degrees.

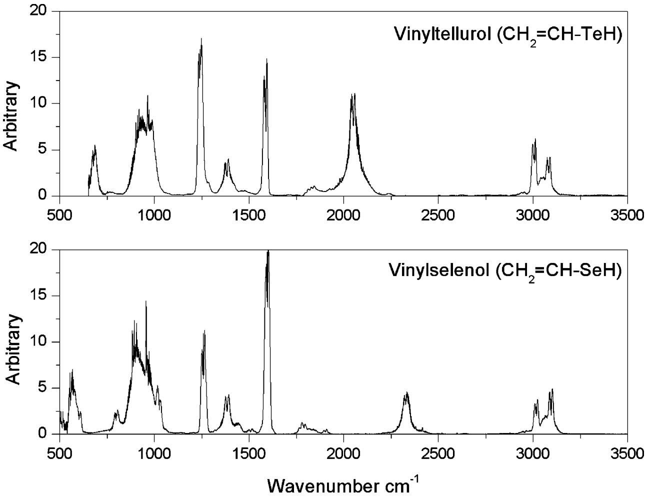

Figure 2. Gas-phase spectra of the studied vinylic compounds. The spectrum of the vinyl selenol was obtained at a temperature of −40 °C with an optical path of 10 m and a typical pressure of 1−1.5 torr. The vinyl tellurol spectrum was obtained at room temperature with an optical path of 136 m which is necessary to compensate for the very weak vapor pressure (~0.02 torr) of the compound.

The relative stability of the two isomers, syn and gauche, is quite critical if an unambiguous assignment of the absorption bands is searched, because the shape of the spectrum clearly depends on the relative abundance of both isomers. Hence, we decided to evaluate their relative energies at the CCSD(T)/Def2-QZVP on the aforementioned B3LYP/Def2-QZVP optimized geometries.

Vibrational Analysis. As mentioned in the Introduction, analyses of structures of the aforementioned vinyl heterocompounds were the subject of several theoretical and experimental microwave studies. The vinyl alcohol was found first in the planar syn conformation[13] and later in the anti conformation,[28] which was also found to be planar. The energy difference between the two conformers was derived from experimental

TABLE 1: Relative Energies and Relative Abundances of the Syn and Gauche Isomers of Vinyl Selenol and Vinyl Tellurol

	$CH_2{=}CH{-}SeH$		$CH_2{=}CH{-}TeH$	
	syn	gauche	syn	gauche
geometry	planar	H atom (SeH) out of plane; CCSeH dihedral angle = 165.4°	planar	H atom (TeH) out of plane; CCTeH dihedral angle = 152.3°
CCSD(T) energy[a]	−2478.913463	−2478.913163	−346.206351	−346.206435
B3LYP Gibbs energy adjustment	0.022226	0.021284	0.01965	0.01948
CCSD(T) Gibbs energy[a]	−2478.891879	−2478.891237	−346.186701	−346.186955
ΔE[b]	0	0.79	0.2	0
ΔG[b]	0	1.7	0.7	0
molar fraction (%)	66[c]	34[c]	43[c]	57[c]
	50[d]	50[d]	28[d]	72[d]

[a] Values in hartrees, obtained with a very extended Def2-QZVP basis set. [b] Values in kJ mol^{-1}. [c] Relative abundances taking into account the values of ΔG for each rotamer. [d] Relative abundances taking into account that for the gauche there are two degenerate forms.

relative intensities (4.5 kJ/mol).[28] The vinyl thiol was also found to exist under two stable conformations: a planar syn and a quasi-planar anti rotamer.[29] As in the case of the vinyl alcohol, the syn form is the lowest energy conformation by about 0.6 kJ mol^{-1}. The barrier between the syn and anti rotamers was found to be 9.6 kJ mol^{-1}. The anti rotamer at equilibrium shows the H atom of the SH group out of plane by an angle of about 25° with a very small energy barrier of 0.15 kJ mol^{-1} between the two degenerated anti forms. Moreover, the analysis of the variations of the rotational constants from the ground state to the torsional excited states[29,30] led to the conclusion that for the anti conformer the barrier to planarity is lower than the energy of the ground torsional state. From this study the anti conformer can then be considered as planar. Vibrational analyses for both rotameric forms for the vinyl thiol were reported by V. Almond et al.[16]

For both vinyl selenol and vinyl tellurol, which are the subject of this study, some previous information about their structure was available, and the photoelectron spectra of both compounds[17,31] were recorded and analyzed. The microwave spectrum of the vinyl selenol was also published.[32] Two conformers of comparable energy were predicted by theoretical calculations for this latter compound: a planar syn conformer and a gauche one. Up to now, attempts to perform a similar microwave study on vinyl tellurol were unsuccessful, but a nonplanar gauche and a planar syn conformer were calculated (MP2/(C, H, cc-pVTZ; Te, SDB-aug-cc-pVQZ) and B3LYP level) to be local minima with an energy difference of only a few tenths of a kilojoule/mole and a rotation barrier of only 4.3 kJ mol^{-1}; therefore, it was concluded that the TeH group rotates almost freely.[31] The photoelectron spectrum, however, was not able to differentiate both conformers.

In the present study, both the B3LYP/6-311+G(3df,2p) and the B3LYP/ Def2-QZVP geometry optimizations agree with the aforementioned results and predict the existence of two rotamers, the syn, which is planar for both compounds, and the nonplanar gauche. The gauche rotamers have two degenerate conformers, which differ by the position of the SeH (TeH) hydrogen atom above or below the molecular plane. It is worth mentioning that the energy barrier connecting these two gauche conformers is extremely low (0.2 kJ mol^{-1} for vinyl selenol and 0.7 kJ mol^{-1} for vinyl tellurol) which means that at room temperature the hydrogen atom is moving freely above and below the plane.

Our results show that the syn conformer is lower in energy than the gauche one in the case of the vinyl selenol, the energy gap being 1.7 kJ mol^{-1}. However, we found an opposite energetic order for the two rotamers of the vinyl tellurol, with a very small energy gap of about 0.7 kJ mol^{-1} in favor of the gauche form. Both forms are interconnected through an internal rotation of the XH group, which for the case of vinyl selenol implies an activation barrier of 7.4 kJ mol^{-1}, which reduces to 5.5 kJ mol^{-1} for vinyl tellurol. In any case, these barriers, although small, are high enough for both rotamers to coexist in the gas phase at room temperature.

It is worth mentioning that the gap between both conformers of vinyl selenol in terms of Gibbs energies, calculated at the CCSD(T)/Def2-QZVP// B3LYP/Def2-QZVP level, is identical to that obtained when the G2 theory is used, so we can have confidence in the reliability of our estimates for vinyl tellurol. From these calculated Gibbs energies, the expected populations in the gas phase should be 66% syn and 34% gauche for vinyl selenol and 43% syn and 57% gauche for vinyl tellurol. These populations became (50% syn, 50% gauche) and (28% syn, 72% gauche) for the −SeH and the −TeH vinylic compounds, respectively, if one takes into account the degeneracy of the gauche conformer.

It is worth noting also that for both vinyl selenol and vinyl tellurol, the harmonic and anharmonic vibrational frequencies calculated at the B3LYP/Def2-QZVP level differ very little from those obtained with the 6-311+G(3df,2p) Pople's basis set. This indicates that, as far as the vibrational frequencies are concerned, our values can be considered as converged.

The optimized geometries of both stereoisomers of the two studied molecules are shown in Figure 1. Their total and relative energies are summarized in Table 1.

Vibrational harmonic and anharmonic calculated frequencies and infrared intensities obtained with extended Def2-QZVP basis set are summarized in Table 2. Equivalent results obtained with the Pople's 6-311+G(3df,2p) basis set are given in Table S1 of the Supporting Information. For both molecules, the predicted values are in very good agreement with the observed spectra. The vibrational modes most sensitive to conformational changes, namely, the in-plane CH bending and the CH_2 rocking and wagging, allowed us to compare the calculated intensities, after their correction by the corresponding molar fraction, with the observed ones. The result of this comparison, as we shall discuss in more detail later, was very satisfactory and reinforced our predictions on the relative stability of both isomers.

Spectroscopic Analysis. ***CH Stretching Region.*** The symmetric and antisymmetric CH_2 stretching modes in vinylic compound series, namely, vinyl alcohol, vinyl thiol, vinyl selenol, and vinyl tellurol, are not sensitive to conformational effects and absorb almost at the same frequency in both conformers. In this series, the CH_2 symmetric stretching absorbs

TABLE 2: Predictions of Harmonic (ω) and Anharmonic (ν) Vibrational Frequencies for the Syn and Gauche Rotamers of Vinyl Selenol and Vinyl Tellurol Calculated at the B3LYP/ Def2-QZVP Level[a]

mode numbering and assignment		rotamer	$CH_2{=}CH{-}SeH$			$CH_2{=}CH{-}TeH$		
			ω (cm^{-1})	ν (cm^{-1})	I_{IR}	ω (cm^{-1})	ν (cm^{-1})	I_{IR}
$\nu_1(a')^b$	CH_2 antisymmetric stretching	syn	3216	3075	6.1	3205	3065	5.8
		gauche	3216	3077	4.8	3202	3060	5.3
$\nu_2(a')$	CH stretching	syn	3164	3031	1.9	3152	3018	4.2
		gauche	3180	3055	1.2	3168	3026	2.1
$\nu_3(a')$	CH_2 symmetric stretching	syn	3134	2961	2.1	3132	2951	3.5
		gauche	3134	2963	2.1	3122	2953	4.6
$\nu_4(a')$	X−H stretching (X = Se, Te)	syn	2400	2310	14.5	2116	2044	43.5
		gauche	2413	2287	12.8	2116	2045	48.3
$\nu_5(a')$	C=C stretching	syn	1646	1612	46.6	1637	1602	35.1
		gauche	1648	1611	56.6	1639	1605	36.3
$\nu_6(a')$	CH_2 scissoring	syn	1428	1393	11.7	1426	1391	13.6
		gauche	1425	1393	12.7	1425	1389	13.7
$\nu_7(a')$	CH in-plane bending	syn	1297	1272	6.9	1281	1254	19.6
		gauche	1286	1261	16.7	1269	1238	33.1
$\nu_8(a')$	CH_2 rocking	syn	1046	1031	17.4	1021	1006	11.8
		gauche	1036	1018	5.6	1019	999	4.8
$\nu_9(a')$	CXH (X = Se, Te) bending	syn	802	823	10.8	685	678	19.5
		gauche	819	811	5.2	692	684	13.5
$\nu_{10}(a')$	C−X (X = Se, Te) stretching	syn	565	559	9.0	494	487	0.9
		gauche	591	577	8.3	528	523	8.3
$\nu_{11}(a')$	C=C−X (X = Se, Te) bending	syn	332	336	1.8	290	292	1.4
		gauche	309	309	0.1	271	270	0.5
$\nu_{12}(a'')$	CH out-of- plane bending	syn	991	968	17.2	995	972	16.6
		gauche	990	965	22.1	996	974	21.4
$\nu_{13}(a'')$	CH_2 wagging	syn	914	902	39.4	932	917	34.0
		gauche	924	889	36.9	946	934	31.6
$\nu_{14}(a'')$	CH_2 twisting	syn	570	656	19.5	526	519	21.9
		gauche	568	567	21.6	514	506	10.5
$\nu_{15}(a'')$	X−H (X = Se, Te) out-of-plane bending	syn	223	245	3.6	167	169	0.0
		gauche	75	70	6.2	101	104	4.5

[a] I_{IR} stands for infrared intensities in km·mol^{-1}. [b] Note that the symmetry assignment of the different absorption bands applies only to the C_s syn rotamer.

at 3122,[14] 3100,[16] 3095, and 3081 cm^{-1}, when one of the hydrogen atoms in ethylene molecule is substituted by an −OH, −HS, −SeH, or −TeH group, respectively. For vinyl selenol and vinyl tellurol, the two bands at 3017 and 3004 cm^{-1}, respectively, were assigned to the CH_2 antisymmetric stretch. A value of 2980 cm^{-1} was reported for the vinyl thiol,[16] and no measured value is available for the vinyl alcohol. Conversely, conformational effects are significant as far as the CH stretching mode is concerned, leading to a difference of frequency between the two rotamers of about 12 cm^{-1}. For vinyl selenol, the bands at 3050 and 3062 cm^{-1} correspond to the syn and gauche rotamers, respectively, whereas for the vinyl tellurol they appear at 3047 and 3060 cm^{-1}. No experimental values are available for the corresponding alcohol, and the same frequency 3030 cm^{-1} was assigned to both syn and anti conformers in the thiol compound.[16] In agreement with the DFT calculations, the intensities of CH_2 and CH stretching vibrations are from moderate to weak in all these vinyl derivatives. As a matter of fact, for the two compounds investigated here, the calculated frequencies and intensities are in very good agreement with the measured values. It is worth noting that the ν_{obs}/ν_{cal} ratio (0.96) is smaller than unity when using calculated harmonic frequencies, but it becomes very close to 1 (1.01) when the calculated anharmonic values are employed.

C=C Stretching Mode. The isolated band associated with the C=C stretching is very characteristic of the vinyl compounds included in the aforementioned series. The highest value is the one reported for the spectrum of the syn vinyl alcohol (1648 cm^{-1}).[12] This vibration appears successively red-shifted for the S- (1602, 1602 cm^{-1}),[16] Se- (1595, 1596 cm^{-1}), and Te- (1585, 1587 cm^{-1}) vinyl derivatives, for both the syn and the gauche forms, respectively. The intensity of this mode is quite similar for the two stereoisomers but decreases on going from oxygen to tellurium. It is very strong for the vinyl alcohol, but its intensity continually decreases to become only moderate for the vinyl tellurol. Frequencies and intensities of this mode are very well reproduced by our calculations.

CH In-Plane Deformation. The CH_2 scissoring movement absorbs at almost the same frequency, 1383 cm^{-1}, for both conformers in all compounds of this vinyl series, with the exception of the anti rotamer vinyl thiol and the syn rotamer of vinyl alcohol, which appear shifted toward higher values (1392 and 1412 cm^{-1}, respectively). Note that this mode constitutes a good indicator for the presence of the $-CH{=}CH_2$ fragment in any gas-phase infrared analyses.

The in-plane CH bending is one of the vibrational modes which presents a larger frequency difference between the two conformers. More importantly, in this series, the in-plane CH bending appears as an isolated band, and therefore a measurement of their relative intensity for the two stereoisomers is feasible. For the vinyl tellurol, the calculated anharmonic frequencies are 1254 and 1238 cm^{-1} with the highest value for the syn form. The respective intensities (harmonic) are 19.6 and 33.1 km·mol^{-1} in a ratio of 1.7 in favor of the gauche form which becomes equal to 4.7 after correction by molar fraction, estimated by the ΔG values reported in Table 1. These values are in excellent agreement with the observed frequencies and intensities ratio (1248, 1240 cm^{-1} and $I_{gauche}/I_{syn} = 5$). For vinyl selenol, the in-plane CH bending mode is predicted at (1272 and 1261 cm^{-1}) and observed at (1265 and 1257 cm^{-1}), the

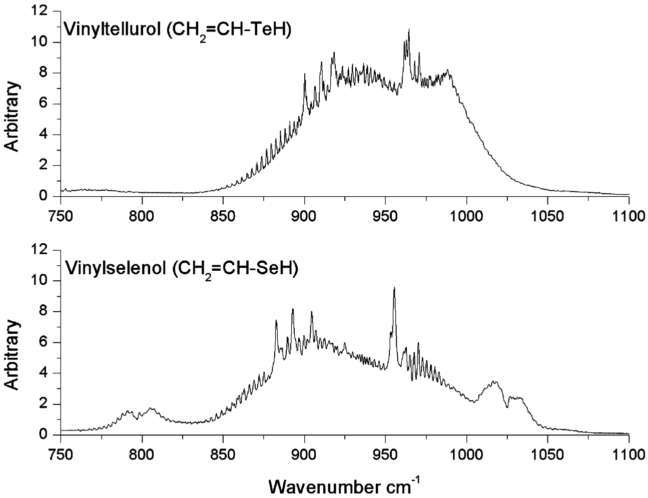

Figure 3. Expanded spectra between 750 and 1100 cm^{-1} of vinyl selenol and tellurol in the gas phase. An equivalent structure was observed in the vinyl thiol spectrum (ref 16).

highest frequency being again that corresponding to the syn form. The reported calculated[18] data for this mode for vinyl thiol are (1286 cm^{-1}, 2 km mol^{-1}) and (1285 cm^{-1}, 11 km mol^{-1}) for the syn and the anti conformers, respectively, while the corresponding experimental[14] values are (1284, 1272 cm^{-1}). For the vinyl alcohol the reported calculated frequencies and intensities[33] were 1319 cm^{-1} and 5 km·mol^{-1} for the syn form, and 1325 cm^{-1}, 8 km·mol^{-1} for the gauche one, although experimentally it was observed only for the syn conformer at 1300 cm^{-1}.[12]

The CH$_2$ rocking, which is the other in-plane CH deformation, is assigned unambiguously at 1026 and 988 cm^{-1} for the syn rotamer of the vinyl selenol and vinyl tellurol, respectively. The corresponding CH$_2$ rocking bands for the gauche rotamers appear red-shifted, by about 10 cm^{-1} (at 1016 and 977 cm^{-1}, respectively) in very good agreement with anharmonic theoretical predictions. The values of 1059 and 1067 cm^{-1} were reported for syn and anti vinyl thiol,[16] respectively, and 943 cm^{-1} for syn vinyl alcohol.[12]

CH Out-of-Plane Deformations. The rotational fine structure may be clearly seen in the C-type bands for CH and CH$_2$ wagging and the CH$_2$ twisting of the vapor-phase spectra of vinyl compounds. The corresponding absorption region, below 1000 cm^{-1} (see Figure 3), comprises a very broad absorption band, to which many fairly sharp peaks and many vibration−rotation fine structure features are superimposed. The adding up of band shapes for a′ and a″ modes and the possible presence of some combination bands make this spectral area by far the most difficult to analyze. However, since the rotational constants for the vinyl selenol are accurately known from previous microwave studies[31] and those for the vinyl tellurol can be obtained from our calculations, it is possible to predict the mean near-prolate top Q branch spacing $2[A - (B + C)/2]$ for both rotamers. Table 3 summarizes the rotational constants and the corresponding spacing for the vinyl compounds under scrutiny as compared with results previously reported for the vinyl alcohol and vinyl thiol.

In the vinyl selenol spectrum, the strong sharp doublets at 962 and 955 cm^{-1} (see Figure 3), whose corresponding overtones appear at 1928 and 1902 cm^{-1}, are attributed to CH bending vibrations of the syn and gauche conformers. The CH$_2$ wagging is predicted to absorb around 890 cm^{-1}. In this region, we observe a very complex structure, with three main peaks at 904, 893, and 882 cm^{-1}. By an analysis of the vibration−rotation fine structure, and taking into account that the corresponding overtones are observed at 1772 and 1788 cm^{-1}, the doublets at 893 and 882 cm^{-1} can be tentatively assigned to the Q branches of the corresponding syn and gauche bands. In the vinyl tellurol spectrum, the observed vibration−rotation fine structure in the same region is similar. Hence, for the syn and the gauche forms, respectively, we have tentatively assigned the couple of values (970, 964 cm^{-1}) and (1935, 1833 cm^{-1}) to δ_{CH} and $2\delta_{\mathrm{CH}}$ and the couple of values (900, 910 cm^{-1}) and (1802, 1819 cm^{-1}) to ω_{CH2} and $2\omega_{\mathrm{CH2}}$. In the observed syn vinyl alcohol, the frequencies reported for CH and CH$_2$ wagging are, respectively, 971 and 814 cm^{-1}. Similarly, these two vibrations appear in the same order (at 954 and 871 cm^{-1} in the syn form and at 958 and 876 cm^{-1} in the anti form) for the S derivative.

Finally, the CH$_2$ twisting is predicted to absorb with medium to strong intensities in all the derivatives of the vinyl series. The highest frequency (698 cm^{-1})[12] was reported for the OH derivative. For the S- and Se-containing compounds, this mode is red-shifted to (586, 600 cm^{-1})[16] and (553, 553 cm^{-1}), respectively, the highest frequency being that of the corresponding syn rotamer. For vinyl tellurol this mode is predicted to absorb at (502, 491 cm^{-1}) and therefore is out of range with regard to experimental accessibility in our study.

Vibrations Implying the Heteroatoms. The stretching vibration of the X−H (X = O, S, Se, Te) group is not sensitive to conformational effects. With the only exception of vinyl selenol, the same frequency is attributed to the two observed rotamers. A frequency of 3620 cm^{-1} with a moderate intensity was reported for the syn vinyl alcohol.[12] Obviously, for the corresponding thiol derivative this mode is significantly shifted to the red (2599 cm^{-1}) with a very weak intensity.[16] For vinyl tellurol, the X−H stretch absorbs at 2047 cm^{-1} with strong intensity. For vinyl selenol, in agreement with our anharmonic predictions, we observe a 10 cm^{-1} splitting between the Se−H stretching vibrations of the two rotamers. We assign frequencies at 2337 and 2327 cm^{-1} to syn and gauche conformers, respectively.

The C−X stretching vibration in these compounds gives rise to a weak absorption band with the only exception being the syn vinyl alcohol for which this band, appearing at 1090 cm^{-1}, is exceptionally very strong. As expected the values reported for vinyl thiol (703 cm^{-1}) and measured by us for vinyl selenol (574 cm^{-1}) are much smaller. The corresponding C−Te stretching frequency for vinyl tellurol is predicted to be 487 cm^{-1} and therefore out of our experimental range. The C−X−H bending mode varies within a wide frequency range along the series. The highest frequency at 1260 cm^{-1} was observed for the OH derivative,[14] whereas the lowest, at 678 cm^{-1}, was found for vinyl tellurol. For the remaining modes, namely, the C=C−X bending and the X−H out-of-plane bending, the experimental values are only available for the vinyl alcohol and vinyl thiol and are summarized in Table 4.

In addition to the clearly identified overtones of the CH and CH$_2$ wagging in the two studied compounds, we have also assigned some non-null combination bands and overtones in the two studied spectra. All these bands are summarized in Table 5.

Conclusions

The infrared spectra of gaseous vinyl selenol and vinyl tellurol have been investigated both experimentally and theoretically. Two conformers, the syn rotamer, which is planar, and a nonplanar gauche rotamer, were found to be local minima for

TABLE 3: Rotational Constants and Rotational Spacings for the Syn and Anti (Gauche) Rotamers of $CH_2{=}CHXH$ (X = O, S, Se, Te) Derivatives

	syn/anti (gauche) rotational constants (MHz)			rotational spacing (cm^{-1}) $2[A - (B + C)/2]$	
	A	B	C	calculated	evaluated
vinyl alcohol[a,b]	59660.78/62868.10	10561.67/10455.81	8965.79/8963.26	3.328/3.546	
vinyl thiol[c]	49815.28/49422.75	5835.72/5897.22	5222.08/5279.44	2.954/2.924	
vinyl selenol [d]	46700.54/45096.78	3968.47/4048.09	3657.23/3725.40	2.86/2.406	2.3(±0.3)/2.3(±0.3)
vinyl tellurol[e]	44064.09/42538.45	3098.36/3141.53	2894.79/2943.96	2.739/2.634	2.6(±0.3)/2.6(±0.3)

[a] Syn values from ref 13. [b] Anti values from ref 28. [c] Syn and anti values from ref 29. [d] Syn and gauche values from ref 32. [e] Syn and gauche values obtained in B3LYP/Def2QZVP calculations.

TABLE 4: Experimental Vibrational Frequencies (cm^{-1}) Assigned in the Infrared Spectra of $CH_2{=}CHXH$ (X = O, S, Se, Te) Compounds[a]

		$CH_2{=}CH{-}OH$	$CH_2{=}CH{-}SH$[e]		$CH_2{=}CH{-}SeH$[f]		$CH_2{=}CH{-}TeH$[f]	
	mode numbering and assignment	syn	syn	anti	syn	gauche	syn	gauche
$\nu_1(a')$	CH_2 asymmetric stretching	3122[c]	3100	3100	3095	3095	3084	3081
$\nu_2(a')$	CH stretching		3030	3030	3050	3062	3047	3060
$\nu_3(a')$	CH_2 symmetric stretching		2980	2980	3016	3017	3004	3004
$\nu_4(a')$	X−H stretching (X = O, S, Se, Te)	3634[c], 3620[d]	2599	2599	2337	2327	2047	2047
$\nu_5(a')$	C=C stretching	1645[c], 1648[d]	1602	1602	1595	1596	1585	1587
$\nu_6(a')$	CH_2 scissoring	1412[c], 1409[d]	1382	1392	1383	1383	1382	1383
$\nu_7(a')$	CH in plane bending	1300[c], 1326[d]	1284	1272	1265	1257	1248	1240
$\nu_8(a')$	CH_2 rocking	948[c], 943[d]	1059	1067	1026	1016	988	977
$\nu_9(a')$	CXH angle bending (X = Se, Te)	1260[c], 1300[d]	883	893	798	798	685	678
$\nu_{10}(a')$	C−X stretching (X = Se, Te)	1098[c], 1090[d]	703	703	574	600		
$\nu_{11}(a')$	C=C−X angle bending (X = Se, Te)	486[d]	376	376				
$\nu_{12}(a'')$	CH out-of plane-bending	971[d]	954	958	962	955	970	964
$\nu_{13}(a'')$	CH_2 wagging	817[c], 814[d]	871	876	893[g]	882[g]	900[g]	910[g]
$\nu_{14}(a'')$	CH_2 twisting	699[c], 698[d]	586	600	553	553		
$\nu_{15}(a'')$	X−H out-of-plane bending (X = Se, Te)	413[d]	155	74				

[a] The syn form is planar in all compounds and is the most stable in the first three compounds. The anti rotamer is planar in the vinyl alcohol and quasi-planar in the vinyl thiol, and the gauche form is nonplanar in the vinyl selenol and vinyl tellurol. [b] Note that the symmetry assignment of the different absorption bands applies only to the C_s syn rotamer [c] From ref 14. [d] From ref 12. [e] From ref 16. [f] This work. [g] Tentatively assigned.

TABLE 5: Frequencies of the Overtones and Combination Bands Measured in the Gas-Phase Infrared Spectra of Vinyl Selenol and Vinyl Tellurol

	$CH_2{=}CH{-}SeH$		$CH_2{=}CH{-}TeH$	
	syn	gauche	syn	gauche
$2\nu_9$	1928	1902	1935	1833
$\nu_{10} + \nu_9$		1831		
$2\nu_{10}$	1772	1788	1802	1819
$\nu_{11} + \nu_9$	1755	1755		
$2\nu_{11}$	1590			
$\nu_{13} + \nu_9$		1507	1469	1469
$\nu_{13} + \nu_{10}$		1447	1415	1415
$\nu_{11} + \nu_{13}$		1269		
$3\nu_{11}$	2379	2379		
$2\nu_7$		2519.7		
$\nu_6 + \nu_7$		2637	2627	2627
$\nu_5 + \nu_6$	2956		2946	2946

both compounds. The activation barrier associated with the rotation of the XH (X = Se, Te) which connects them is rather low, but still high enough for the two isomers to be observable at room temperature. The gauche rotamer presents two degenerate conformers, which differ by the position of the SeH (TeH) hydrogen atom, above or below the molecular plane. Both isomers are connected through very low activation barriers, so they should interchange very rapidly at room temperature. Our theoretical results are in good agreement with the main features of the experimental spectra. Fundamental bands and some combination bands of vinyl selenol and vinyl tellurol were assigned and compared with the vinyl alcohol and the vinyl thiol belonging to the same vinylic series.

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Supporting Information Available: Harmonic and anharmonic vibrational frequencies for the syn and gauche rotamers of vinyl selenol and vinyl tellurol calculated at the B3LYP/6-311+G(3df,2p) level. This material is available free of charge via the Internet at http://pubs.acs.org

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