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Implications of Intramolecular OH···Se Hydrogen Bonding and CH···O Interaction in the Conformational Stabilization of 2-(Methylseleno)ethanol Studied by Vibrational Spectroscopy and Density Functional Theory

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The conformational stability of 2-(methylseleno)ethanol has been studied by vibrational spectroscopy and density functional theory. In an argon matrix, the molecules assume primarily the gauche$^{\pm}$−gauche$^{\pm}$−gauche$^{\mp}$ (GGg′) and gauche$^{\mp}$−gauche$^{\pm}$−gauche$^{\mp}$ (G′Gg′) conformations around the $CH_3Se-CH_2-CH_2-OH$ bonds, being consistent with the theoretical energies of the conformers. The GGg′ and G′Gg′ conformers are stabilized by intramolecular OH···Se hydrogen bonding. The conformational stabilization energy by this hydrogen bonding was estimated by density functional calculations as 14.5 kJ mol^{-1}, which is substantially the same as the corresponding energies for OH···O and OH···S hydrogen bonding. These experimental and theoretical results show that intramolecular OH···Se hydrogen bonding is as strong as OH···O and OH···S hydrogen bonding. An additional intramolecular CH···O interaction with its stabilization energy 5.6 kJ mol^{-1} stabilizes the G′G conformation around the $CH_3Se-CH_2-CH_2OH$ bonds. The spectral observation that the wavenumbers of the hydrogen-bonded O−H stretching mode for 2-(methylseleno)ethanol and the thio-analogue are significantly lower than the wavenumber for the oxy-analogue was also discussed.

Introduction

The conformation of molecules is important in molecular sciences, in particular, in relation to the emergence of relevant functions of the molecular system. It has been established that, among a number of factors, intramolecular and intermolecular interactions play an important role in determining the conformation of the molecule. Hydrogen bonding has long been known as one of the crucial interactions that stabilize particular conformations of many organic and biological molecules.[1] Recent studies have shown that new types of hydrogen-involved weaker interactions play an important role in the conformational stabilization of molecules.[2−6]

To elucidate conformational implications of intramolecular hydrogen bonding, we have studied the conformations of 2-methoxyethanol ($CH_3OCH_2CH_2OH$)[7] and 2-(methylthio)ethanol ($CH_3SCH_2CH_2OH$)[8] by matrix-isolation infrared spectroscopy. In these studies, we have shown that the molecules in the matrix-isolated state assume only the conformations stabilized by intramolecular hydrogen bonding, OH···O or OH···S. It was also shown on the basis of density functional calculations that the conformational stabilization energy by the formation of OH···S hydrogen bonding is substantially the same as the corresponding energy by the formation of OH···O hydrogen bonding.[9] The results of these previous studies indicate that intramolecular hydrogen bonding is strong enough to be a dominant factor determining the molecular conformation in the isolated state.

In addition to the generally accepted intramolecular hydrogen bonding such as OH···O or OH···S, a new type of intramolecular attractive interaction between a hydrogen atom in the methyl or methylene group and an oxygen atom, i.e., CH···O interaction, has now been well recognized as an important interaction that determines the molecular conformation.[2−5] This interaction was experimentally evidenced for the relevant conformers of 1,2-dimethoxyethane ($CH_3OCH_2CH_2OCH_3$)[2] and 1-methoxy-2-(methylthio)ethane ($CH_3OCH_2CH_2SCH_3$)[5] in the matrix-isolated state. The same interaction deserves considering in the conformational stabilization of 2-methoxyethanol and 2-(methylthio)ethanol. The previous studies on these compounds have in fact shown that intramolecular CH···O interaction competes with OH···O or OH···S hydrogen bonding in determining the conformation.[7,8] A distinctive property of this attractive interaction is the shortening of the relevant C−H bond,[8,10−14] being different from the lengthening of the O−H bond on the formation of OH···O or OH···S hydrogen bond.

To gain a further insight into the implications of possible intramolecular interactions in the conformational stabilization of a series of $CH_3XCH_2CH_2OH$ compounds, we have investigated in this work the conformation of 2-(methylseleno)ethanol ($CH_3SeCH_2CH_2OH$), a compound that contains a heteroatom X of a higher-periodic element selenium, by matrix-isolation infrared spectroscopy and density functional theory. The Raman spectra of this compound in the liquid and solid states were also studied for comparison of the conformational relevance of intramolecular and intermolecular interactions in different phases.

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Experimental Section

2-(Methylseleno)ethanol was prepared by reacting bis(2-hydroxyethyl) diselenide with sodium tetrahydroborate and then with dimethyl sulfate in absolute ethanol under nitrogen atmosphere at 0 °C.[15] Bis(2-hydroxyethyl) diselenide was prepared by treating the mixture of powdered sodium hydroxide, selenium, and *N*,*N*-dimethylformamide with hydrazine hydrate and then with 2-bromoethanol.[16,17] The crude products of bis-(2-hydroxyethyl) diselenide and 2-(methylseleno)ethanol were purified by column chromatography on silica gel (hexane/ethyl acetate = 4/1).

The infrared spectra of 2-(methylseleno)ethanol in an argon matrix were measured with a JASCO FT/IR-350 Fourier transform spectrometer using a deuterated triglycine sulfate (DTGS) detector. Premixed gas of argon/2-(methylseleno)-ethanol = 2000 was slowly sprayed and deposited onto a cesium iodide plate cooled to 11 K by an Iwatani CryoMini D105 refrigerator. The spectra were obtained by coaddition of 100 scans at a resolution of 1 cm^{-1}. To study the spectral changes with increasing temperature, the deposited sample was annealed at different temperatures up to 41 K and was subsequently cooled back to 11 K to measure the spectra. The Raman spectra in the liquid state at various temperatures and in the solid state at 77 K were recorded on a JASCO NR-1800 Raman spectrometer equipped with a Princeton Instruments CCD detector. An NEC argon ion laser GLG 2162 operating at 514.5 nm was used for excitation.

Calculations

The density functional calculations of the energies, structural parameters, and vibrational wavenumbers for 12 optimized conformers of 2-(methylseleno)ethanol were performed by using Becke's three-parameter hybrid functional[18] combined with the Lee−Yang−Parr correlation functional[19] (B3LYP). The basis set used was 6-311+G**. The optimized structures of the 12 conformers are depicted in Figure 1. The calculation failed the optimization of geometries for the TGg′ and GGg conformers. The density functional calculations were carried out with the GAUSSIAN 98 program.[20] The input data for the GAUSSIAN 98 program were prepared by using the graphical molecular modeling program Molda.[21] The calculated vibrational wavenumbers were scaled by the wavenumber-linear scaling (WLS) method using a relationship proposed previously.[22] The B3LYP/6-311+G** calculations were also performed on several selected conformers of 2-methoxyethanol and 2-(methylthio)ethanol.

Results and Discussion

Energies of Conformers. The relative energies of 12 optimized conformers of 2-(methylseleno)ethanol (MSE) calculated by the B3LYP/6-311+G** method are given in Table 1, where the intramolecular interactions involved are indicated for the relevant conformers. The molecular conformation of MSE is designated for a sequence of the three bonds $CH_3Se-CH_2-CH_2-OH$ by the symbols T or t for trans, G or g for gauche$^{\pm}$, and G′ or g′ for gauche$^{\mp}$, and the lower-case symbols apply to the conformation around the CH_2CH_2-OH bond.

The calculated results indicate that the most stable conformer of MSE is GGg′ and the second most stable conformer is G′Gg′ with an energy 3.2 kJ mol^{-1} higher than the energy of GGg′. These two conformers are stabilized by intramolecular hydrogen bonding between the hydroxyl hydrogen atom and the selenium atom (OH···Se). The conformational stabilization energy by OH···Se hydrogen bonding can be estimated as an energy difference between the non-hydrogen-bonded conformer GGg and the hydrogen-bonded conformer GGg′, as only the sign of the gauche for the CH_2CH_2-OH bond is different from each other in these conformers. Since the minimum-energy geometry of the GGg conformer was not attained, the energies of the GG[τ] conformation with varying torsion angle τ around the CH_2CH_2-OH bond were calculated. For each conformation with a fixed value of τ, the molecular geometry was optimized to yield the minimized energy. The energy curve thus obtained for the GG[τ] conformation is shown in Figure 2, where the energy curve for the GG[τ] conformation of 2-(methylthio)-ethanol (MTE), for which the GGg′ conformer is the most stable,[8,9] and the energy curve for the TG[τ] conformation of 2-methoxyethanol (ME), for which the TGg′ conformer is the most stable,[7,9] are also shown.

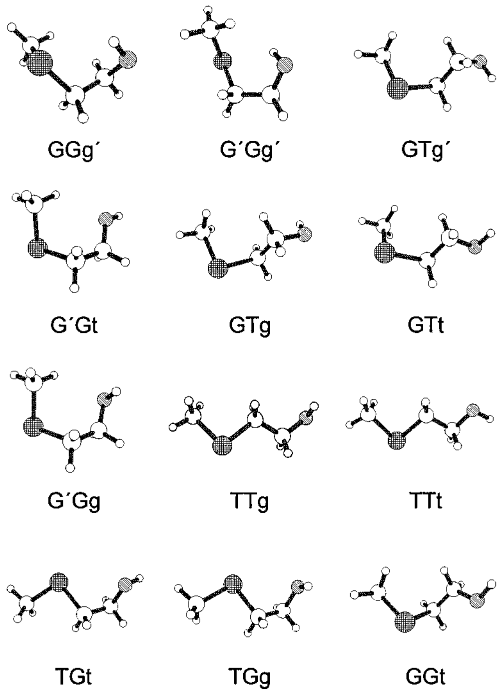

Figure 1. Optimized structures of 12 conformers of 2-(methylseleno)-ethanol. Minimum-energy geometries for the TGg′ and GGg conformers were not attained. The atoms shown hatched are oxygen and the atoms shown crosshatched are selenium.

TABLE 1: Relative Energies of Conformers of 2-(Methylseleno)ethanol Calculated by the B3LYP/6-311+G Method**

conformer	relative energy[a] (kJ mol^{-1})	interaction involved[b]
GGg′	0.000	OH···Se
G′Gg′	3.169	OH···Se, CH···O
GTg′	6.834	
G′Gt	7.657	CH···O
GTg	7.691	
GTt	7.924	
G′Gg	10.691	CH···O
TTg	10.710	
TTt	11.369	
TGt	12.266	
TGg	12.353	
GGt	13.288	
TGg′	*c*	
GGg	*c*	

[a] Relative energy with respect to the energy of the GGg′ conformer. [b] OH···Se, intramolecular OH···Se hydrogen bonding; CH···O, intramolecular 1,5-CH···O interaction. [c] Minimum-energy geometry was not attained.

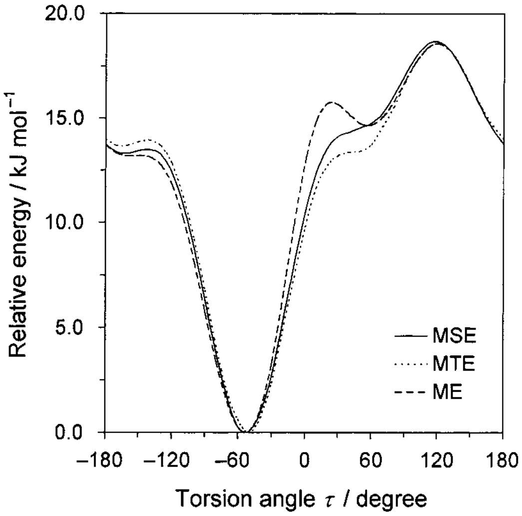

Figure 2. Energy curves for the GG[τ] conformation of 2-(methylseleno)ethanol (MSE), the GG[τ] conformation of 2-(methylthio)ethanol (MTE), and the TG[τ] conformation of 2-methoxyethanol (ME), with varying torsion angle τ around the CH_2CH_2-OH bond.

The energy curve for the GG[τ] conformation of MSE shows a deep minimum at $\tau = -54°$ corresponding to the most stable conformation GGg′ and a shallow hollow at $\tau \approx 50°$ corresponding to the unoptimized conformation GGg. The conformational stabilization energy by OH···Se hydrogen bonding is obtained as 14.5 kJ mol^{-1} as the difference of energies at $\tau \approx 50°$ (GGg) and $-54°$ (GGg′). The energy curves for MTE and ME give the conformational stabilization energies by OH···S and OH···O hydrogen bonding as 13.4 and 14.7 kJ mol^{-1}, respectively, as the energy difference between the GGg and GGg′ conformations for MTE and between the TGg and TGg′ conformations for ME. It is shown from these conformational stabilization energies that OH···Se hydrogen bonding is as strong as OH···O or OH···S hydrogen bonding. This remarkable finding is manifested by the spectral observation, as described later, that MSE molecules in an argon matrix assume primarily the GGg′ and G′Gg′ conformations stabilized by OH···Se hydrogen bonding.

It is important to note that the G′Gt conformer is more stable than the GGt conformer by 5.6 kJ mol^{-1}. In these conformers, the $CH_3Se-CH_2CH_2$ bond and the $SeCH_2-CH_2OH$ bond are in the gauche conformation, but the signs of the two gauche conformations are different in the G′Gt conformer and are the same for the GGt conformer, with the CH_2CH_2-OH bond in common in the trans conformation. Therefore, the stabilization energy for the G′Gt conformer, 5.6 kJ mol^{-1}, is considered to be associated with an interaction specific to the G′G conformation around the $CH_3Se-CH_2-CH_2OH$ bonds. The stabilization of the G′G conformation arises obviously from 1,5-CH···O interaction, which has been evidenced for 1,2-dimethoxyethane[2] and 1-methoxy-2-(methylthio)ethane.[5] The stabilization of the G′G conformation around $CH_3S-CH_2-CH_2OH$ bonds in MTE has also been explained by this interaction.[8] A comparison of the stabilization energies of MSE by OH···Se hydrogen bonding (14.5 kJ mol^{-1}) and CH···O interaction (5.6 kJ mol^{-1}) indicates that the contribution of OH···Se hydrogen bonding to the conformational stabilization is much larger than that of CH···O interaction.

The results of calculations (Table 1) show that the gauche conformation is more stable than the trans conformation around the $CH_3Se-CH_2CH_2$ bond. This is the same propensity as found for the $CH_3S-CH_2CH_2$ bond of MTE.[8] The calculated results also show that for the $SeCH_2-CH_2OH$ bond the trans conformation is intrinsically more stable than the gauche conformation, but in cases where OH···Se hydrogen bonding or CH···O interaction is involved the conformation around this bond is impelled to assume the gauche conformation as described above. This conformational property of the $SeCH_2-CH_2OH$ bond is similar, more or less, to that of the SCH_2-CH_2OH and OCH_2-CH_2OH bonds.

Molecular Geometries. The bond lengths and nonbonded interatomic distances for the 12 optimized conformers of MSE calculated by the B3LYP/6-311+G** method are given in Table 2. The O−H bond lengths for the GGg′ and G′Gg′ conformers are longer than those for other conformers by 0.004−0.005 Å. This lengthening of the O−H bond is obviously due to the formation of OH···Se hydrogen bond. The OH···Se nonbonded interatomic distance in the GGg′ conformer is shorter than the corresponding distance in the G′Gg′ conformer. This implies that the hydrogen bonding in the GGg′ conformer is stronger than that in the G′Gg′ conformer, being consistent with the higher conformational stability of the GGg′ conformer.

The lengths of the C−H bonds associated with 1,5-CH···O interaction are shorter than the lengths of other C−H bonds by 0.003−0.004 Å. The mechanism of this bond shortening has been theoretically studied.[10−14] It was shown that the bond shortening originates from the redistribution of electron density in the C−H bond, induced when the bond comes close to a proton acceptor.[12] The geometry of the G′Gg′ conformer, in which 1,5-CH···O interaction and OH···Se hydrogen bonding are simultaneously involved, is peculiar in that the shortening of the relevant C−H bond is less prominent than that in the G′Gt and G′Gg conformers, and the CH···O nonbonded interatomic distance is much larger than that in the G′Gt and G′Gg conformers. These structural features of the G′Gg′ conformer indicate that the two interactions, 1,5-CH···O interaction and OH···Se hydrogen bonding, compete with each other, leading to diminished conformational stabilization by each of the interactions. It is noted, however, that the co-added effect of both interactions yet makes the G′Gg′ conformer considerably stable, being next to the most stable GGg′ conformer. A similar conformational property has also been observed for the G′Gg′ conformer of MTE.[8]

Matrix-Isolation Infrared Spectra and Molecular Conformation. The matrix-isolation infrared spectra in the 850−1500 cm^{-1} region of MSE annealed at different temperatures are shown in Figure 3, where the calculated spectra of the most stable three conformers, GGg′, G′Gg′, and GTg′, are also shown. The observed and calculated wavenumbers and the vibrational assignments for the GGg′ and G′Gg′ conformers are given in Tables 3 and 4. The wavenumbers calculated by density functional theory of B3LYP/6-311+G** were scaled by the WLS method,[22] which has been shown to give excellent agreement of the calculated wavenumbers with the experimental wavenumbers for a large number of organic and inorganic compounds.[23]

On annealing the matrix sample at 35 K, all of the observed bands become sharper, but their relative intensities do not change substantially. The well-defined bands at 920, 1069, 1072, 1162, 1256, and 1389 cm^{-1} are closely correlated to the normal vibrations of the GGg′ conformer. Although the calculated spectrum of the G′Gg′ conformer is similar in general to that of the GGg′ conformer, the observed bands at 924, 1065, 1157, and 1386 cm^{-1}, which are weaker than the corresponding bands for the GGg′ conformer, are unambiguously assigned to the G′Gg′ conformer. Most of the other bands observed in the

TABLE 2: Bond Lengths and Nonbonded Interatomic Distances for Conformers of 2-(Methylseleno)ethanol

structural parameter	GGg′	G′Gg′	GTg′	G′Gt	GTg	GTt	G′Gg	TTg	TTt	TGt	TGg	GGt
					Bond Lengths[a] (Å)							
O−H	0.9673	0.9668	0.9627	0.9616	0.9626	0.9621	0.9625	0.9627	0.9620	0.9615	0.9630	0.9610
C−H (CH_3)	1.0894	1.0881[b]	1.0894	1.0863[b]	1.0897	1.0894	1.0865[b]	1.0892	1.0893	1.0895	1.0896	1.0897
	1.0886	1.0889	1.0885	1.0893	1.0885	1.0886	1.0899	1.0893	1.0893	1.0898	1.0897	1.0896
	1.0896	1.0898	1.0897	1.0901	1.0897	1.0898	1.0901	1.0896	1.0896	1.0900	1.0898	1.0899
					Nonbonded Interatomic Distances[a] (Å)							
OH···Se	2.7503	2.7672										
CH···O		3.1656		2.5776			2.6237					

[a] Calculated by the B3LYP/6-311+G** method. [b] C−H bond associated with intramolecular 1,5-CH···O interaction.

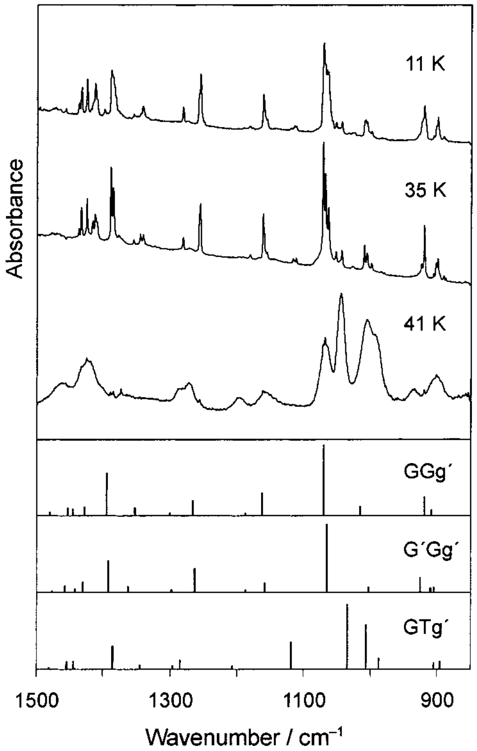

Figure 3. Infrared spectra in the 850−1500 cm^{-1} region of 2-(methylseleno)ethanol in an argon matrix annealed at 11, 35, and 41 K, and the calculated spectra of the GGg′, G′Gg′, and GTg′ conformers.

TABLE 3: Observed and Calculated Wavenumbers in the 850−3600 cm^{-1} Region[a] and Vibrational Assignments for the GGg′ Conformer of 2-(Methylseleno)ethanol

ν_{obs}[b] (cm^{-1})	ν_{calc}[c] (cm^{-1})	vibrational assignment[d]
3528 m	3549	O−H stretch (100)
	1481	C_bH_2 scissor (99)
1433 m	1454	CH_3 ip-asym deform (95)
1425 m	1446	CH_3 op-asym deform (92)
1413 w	1428	C_aH_2 scissor (92)
1389 m	1395	C_bH_2 wag (70), C−O−H bend (21)
1346 w, 1341w	1353	C_bH_2 twist (34), C−O−H bend (26), C_bH_2 wag (24)
1282 w	1301	CH_3 sym deform (100)
1256 m	1266	C_aH_2 wag (55), C_bH_2 twist (15), C−O−H bend (10)
1182 vw	1188	C_aH_2 twist (62), C_bH_2 rock (7)
1162 m	1163	C_bH_2 twist (42), C_aH_2 wag (31), C−O−H bend (30)
1072 s, 1069 s	1071	C−O stretch (74), C−C stretch (30), C−O−H bend (8)
1011 w, 1007 w	1016	C_bH_2 rock (34), C_aH_2 twist (20), C_aH_2 rock (15)
920 m	919	C_bH_2 rock (33), C−C stretch (32), C_aH_2 wag (7)
900 w	909	CH_3 ip-rock (46), CH_3 op-rock (37)
891 vw	906	CH_3 op-rock (57), CH_3 ip-rock (22), C−C stretch (7)

[a] Wavenumbers of the C−H stretching mode are omitted from the table. [b] Observed wavenumbers for an argon matrix. Approximate relative intensities: s, strong; m, medium; w, weak; vw, very weak. [c] Calculated by the B3LYP/6-311+G** method and scaled by the WLS method.[22] [d] Vibrational assignment for $CH_3SeC_aH_2C_bH_2OH$ is given in terms of the group coordinates. Key: sym, symmetric; asym, asymmetric; ip, in-plane; op, out-of-plane. Potential energy distributions (%) evaluated from the B3LYP/6-311+G** calculations are shown in parentheses.

matrix-isolated state are assigned to either or both of the GGg′ and G′Gg′ conformers (Figure 3). The weak bands at 985, 1044, and 1113 cm^{-1} are assigned, however, to neither GGg′ nor G′Gg′. These bands are well correlated to the vibrations of the GTg′ conformer with their calculated wavenumbers, 988, 1036, and 1120 cm^{-1}, respectively. These interpretations of the matrix-isolated spectra in the 850−1500 cm^{-1} region show that the GGg′ and G′Gg′ conformers are the dominant conformers in the matrix-isolated state. The GTg′ conformer also exists as one of the less populated conformers.

On heating the sample up to 41 K, the spectrum becomes broadened and new bands appear at 994, 1006, 1045, and 1198 cm^{-1}, etc. The broadened spectral feature is ascribed to the formation of aggregates of molecules resulting from the loosening of the matrix lattice in the heating process. The new bands are assigned to other conformers than GGg′ and G′Gg′.

The matrix-isolation infrared spectrum of MSE in the O−H stretching region shows two distinct bands at 3528 and 3538 cm^{-1}. These wavenumbers well correspond to the wavenumbers of O−H stretching vibrations of intramolecular hydrogen bonds.[24] The normal coordinate calculations show that the bands at 3528 and 3538 cm^{-1} are correlated to the calculated wavenumbers 3549 cm^{-1} for the GGg′ conformer and 3557 cm^{-1} for the G′Gg′ conformer, respectively (Tables 3 and 4). The wavenumber difference between the two conformers is 10 cm^{-1} in the spectral observation and is 8 cm^{-1} in the calculation, supporting the present assignment of the bands. These results ensure that the conformers with intramolecular OH···Se hydrogen bonding, namely, GGg′ and G′Gg′, exist in the matrix-isolated state. In addition to the two bands discussed above, an O−H stretching band is observed at 3649 cm^{-1}, which is assigned to free O−H stretching vibrations.[24] This spectral observation indicates the existence of conformer(s) without hydrogen bonding. The spectral features in the O−H stretching region are all consistent with the features in the 850−1500 cm^{-1} region with respect to the molecular conformation.

Raman Spectra in the Liquid and Solid States. The Raman spectra in the 400−850 cm^{-1} region of MSE in the liquid and solid states are shown in Figure 4. The observed and calculated wavenumbers and the vibrational assignments in this region are given in Table 5. Since the C−Se stretching wavenumbers are sensitive to the conformation,[25−28] the observed wavenumbers of MSE are examined in relation to the conformation around

TABLE 4: Observed and Calculated Wavenumbers in the 850−3600 cm^{-1} Region[a] and Vibrational Assignments for the G′Gg′ Conformer of 2-(Methylseleno)ethanol

ν_{obs}[b] (cm^{-1})	ν_{calc}[c] (cm^{-1})	vibrational assignment[d]
3538 w	3557	O−H stretch (100)
	1477	C_bH_2 scissor (100)
1437 w	1458	CH_3 ip-asym deform (95)
1425[e] m	1443	CH_3 op-asym deform (93)
1417 w	1431	C_aH_2 scissor (90)
1386 m	1393	C_bH_2 wag (75), C−O−H bend (18)
1355 vw	1364	C_bH_2 twist (34), C−O−H bend (28), C_bH_2 wag (21)
1282[e] w	1298	CH_3 sym deform (101)
1256[e] m	1264	C_aH_2 wag (52), C_bH_2 twist (20), C−O−H bend (11)
1182[e] vw	1189	C_aH_2 twist (56), C_aH_2 wag (12), C−C stretch (7)
1157 w	1159	C_bH_2 twist (39), C_aH_2 wag (29), C−O−H bend (24)
1065 m	1066	C−O stretch (71), C−C stretch (30), C−O−H bend (10)
1000 w	1004	C_bH_2 rock (32), C_aH_2 twist (23), C_aH_2 rock (15)
924 w	926	C_bH_2 rock (33), CH_3 ip-rock (24), C−C stretch (18)
903 w	910	CH_3 op-rock (94)
888 vw	905	CH_3 ip-rock (51), C−C stretch (24), C−O stretch (9)

[a] Wavenumbers of the C−H stretching mode are omitted from the table. [b] Observed wavenumbers for an argon matrix. Approximate relative intensities: m, medium; w, weak; vw, very weak. [c] Calculated by the B3LYP/6-311+G** method and scaled by the WLS method.[22] [d] Vibrational assignment for $CH_3SeC_aH_2C_bH_2OH$ is given in terms of the group coordinates. Key: sym, symmetric; asym, asymmetric; ip, in-plane; op, out-of-plane. Potential energy distributions (%) evaluated from the B3LYP/6-311+G** calculations are shown in parentheses. [e] Assigned also to the GGg′ conformer.

the $CH_3Se-CH_2-CH_2OH$ bonds. The C−Se stretching bands are observed at 568, 595, and 675 cm^{-1} in the liquid state, but the first band disappears on solidification. For methyl propyl selenide ($CH_3SeCH_2CH_2CH_3$), the bands observed in the liquid state at 559, 576, 646, and 660 cm^{-1} were assigned to the Se−CH_2 stretching mode of the GG, TG, GT, and TT conformations, respectively, around the $CH_3Se-CH_2-CH_2CH_3$ bonds, and the band at 591 cm^{-1} was assigned to the CH_3−Se stretching mode.[26] In light of the previous assignments for methyl propyl selenide and of the results of the present normal coordinate analysis, the band at 568 cm^{-1} for MSE is assigned to the Se−CH_2 stretching mode of the GG and G′G conformations around the $CH_3Se-CH_2-CH_2OH$ bonds and the band at 675 cm^{-1} is assigned to the same mode of the GT and TT conformations. A band that can be assigned to the Se−CH_2 stretching mode of the TG conformation was not observed for MSE. The strong band at 595 cm^{-1} is assigned to the CH_3−Se stretching mode of all possible conformations.

In the liquid state, other conformation-sensitive bands are observed at 458, 740, and 795 cm^{-1}. The first band is assigned to the C−C−O bending mode of the GG and G′G conformations around the $CH_3Se-CH_2-CH_2OH$ bonds, the second band to the (Se)CH_2 rocking mode of the GT conformation, and the last to the (Se)CH_2 rocking mode of the GG, G′G, and TT conformations. On decreasing temperature, the relative intensities of the bands at 675 cm^{-1} (Se−CH_2 stretching) and 740 cm^{-1} [(Se)CH_2 rocking] increase, indicating that the GTx conformer is the most stable in the liquid state, where x denotes t, g, or g′. In the solid state, only the GTx conformer exists, as evidenced by the observation of the bands at 596, 677, and 738 cm^{-1} and missing of the other bands.

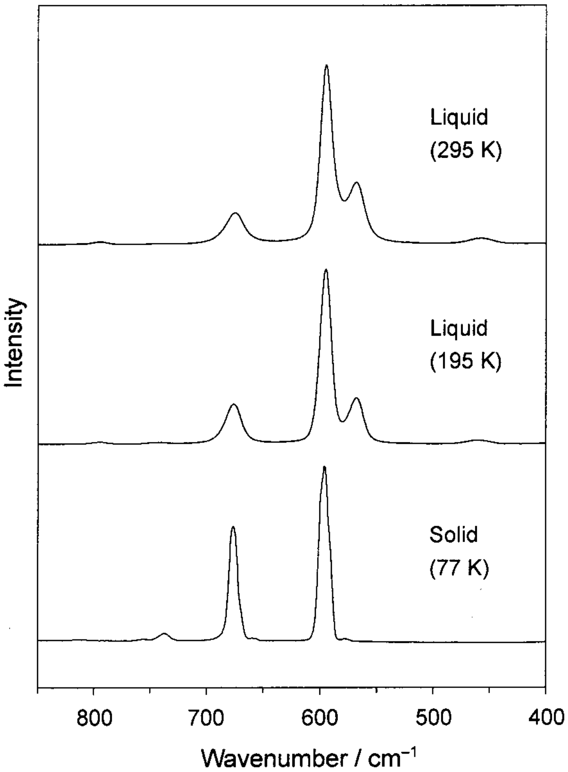

Figure 4. Raman spectra in the 400−850 cm^{-1} region of 2-(methylseleno)ethanol in the liquid state at 195 and 295 K and the solid state at 77 K.

The above discussions show that the conformational stabilization of MSE in the liquid and solid states is remarkably different from that in the matrix-isolated state. This difference implies that the effect of intramolecular OH···Se hydrogen bonding, along with 1,5-CH···O interaction, is a dominant factor in the conformational stabilization in the isolated state, while intermolecular interactions such as OH···O and OH···Se hydrogen bonding are more important than intramolecular interactions in the condensed phases.

Wavenumbers of Intramolecular Hydrogen-Bonded O−H Stretching Mode. The O−H stretching wavenumber has been considered as a measure of the strength of hydrogen bonding.[24,29] For discussing the stabilization energy by hydrogen bonding, the observed and calculated wavenumbers of the O−H stretching mode for MSE are compared with those for MTE and ME in Table 6, where the O−H bond lengths and O−H···X angles (X = Se, S, or O) are also given. The most stable conformers of MSE, MTE, and ME in the isolated state, namely, GGg′, GGg′, and TGg′, respectively, are stabilized by intramolecular OH···X hydrogen bonding. The relevant data for non-hydrogen-bonded conformers, GGt, GGt, and TGt of MSE, MTE, and ME, respectively, are also given in Table 6. These conformers were chosen as the reference conformers by reason that they assume the same conformation around the $CH_3X-CH_2-CH_2$-OH bonds as the hydrogen-bonded conformers but assume the trans conformation around the CH_2CH_2−OH bond instead of gauche$^{\mp}$ in the hydrogen-bonded conformers.

The calculated results show that, for the conformers in which intramolecular OH···X hydrogen bonding is not involved, the O−H stretching wavenumbers and the O−H bond lengths are substantially the same for MSE (X = Se), MTE (X = S), and ME (X = O). For the conformers with intramolecular hydrogen bonding involved, on the other hand, the O−H stretching wavenumber of MSE is significantly lower than the wavenumber of ME and is only slightly lower than the wavenumber of MTE,

TABLE 5: Observed and Calculated Wavenumbers in the 400−850 cm^{-1} Region and Vibrational Assignments for Conformers of 2-(Methylseleno)ethanol

ν_{obs}^{a} (cm^{-1})		ν_{calc}^{b} (cm^{-1})												
liquid	solid	GGg′	G′Gg′	GTg′	G′Gt	GTg	GTt	G′Gg	TTg	TTt	TGt	TGg	GGt	vibrational assignment^c
795 vw		801	796		794			794	775	784			795	C_aH_2 rock
740 vw	738 w			743		742	751							C_aH_2 rock
675 w	677 m			662		663	668		676	683				Se−CH$_2$ stretch
											584	588		Se−CH$_2$ stretch
595 s	596 s	579	578	577	579	577	578	579	580	582	574	577	579	CH$_3$−Se stretch
568 w		552	565		555			550					549	Se−CH$_2$ stretch
458 vw		469	469		437			450			441	452	444	C−C−O bend

[a] Approximate relative intensities: s, strong; m, medium; w, weak; vw, very weak. [b] Calculated by the B3LYP/6-311+G** method and scaled by the WLS method.[22] [c] Vibrational assignment for $CH_3SeC_aH_2C_bH_2OH$ is given in terms of the group coordinates.

TABLE 6: Observed and Calculated O−H Stretching Wavenumbers, O−H Bond Lengths, and O−H···X Angles for 2-(Methylseleno)ethanol (MSE; X = Se), 2-(Methylthio)ethanol (MTE; X = S), and 2-Methoxyethanol (ME; X = O)

	intramolecular hydrogen bonded			non-hydrogen bonded		
property	MSE GGg′	MTE GGg′	ME TGg′	MSE GGt	MTE GGt	ME TGt
ν_{obs} (cm^{-1})	3528	3537	3625			
ν_{calc}^{a} (cm^{-1})	3549	3556	3607	3648	3647	3651
O−H bond length^a (Å)	0.9673	0.9669	0.9643	0.9610	0.9611	0.9607
O−H···X angle^a (deg)	116.2	115.2	106.1			

[a] Calculated by the B3LYP/6-311+G** method. Wavenumbers were scaled by the WLS method.[22]

although the stabilization energy by hydrogen bonding is almost the same for the three compounds as discussed in a preceding section. It is also noted that the lengthening of the O−H bond on the formation of hydrogen bond in MSE and MTE is larger than in ME by about 0.003 Å. The O−H···X angles in MSE and MTE are larger than the angle in ME by 9−10°. These geometrical properties are consistent with the significantly lower wavenumbers of the hydrogen-bonded O−H stretching mode for MSE and MTE than for ME. It is shown, therefore, that the lowering of the O−H stretching wavenumbers for the hydrogen-bonded conformers of MSE and MTE is not immediately correlated to the stabilization energy by the relevant hydrogen bonding.

Conclusions

Implications of intramolecular interactions in the conformational stabilization of MSE have been studied by vibrational spectroscopy and density functional theory. The density functional calculations gave the conformational stabilization energy by intramolecular OH···Se hydrogen bonding as 14.5 kJ mol^{-1}, which is substantially the same as the corresponding energies for OH···O and OH···S hydrogen bonding. The analysis of infrared spectra showed that the MSE molecules in an argon matrix assume primarily the GGg′ and G′Gg′ conformations with intramolecular OH···Se hydrogen bonding. This spectral finding accords with the theoretically predicted stabilization energy by the hydrogen bonding. The conformers of MTE and ME present in the matrix-isolated state are also stabilized by intramolecular OH···S and OH···O hydrogen bonding. We conclude, on the basis of the experimental and theoretical results, that intramolecular OH···Se hydrogen bonding is as strong as OH···O and OH···S hydrogen bonding. In addition to intramolecular OH···Se hydrogen bonding, intramolecular CH···O attractive interaction plays an important role as a secondary interaction in the conformational stabilization of MSE. The stabilization energy by this interaction was estimated to be 5.6 kJ mol^{-1}. The properties of OH···Se hydrogen bonding as revealed in this work should be important for elucidating conformational problems in molecular systems that contain selenium atoms.

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