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The C-Se Stretching Vibrations and Molecular Conformations of Dialkyl Selenides

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Synopsis. The Raman spectra of dialkyl selenides were measured in the liquid and solid states. The most intense Raman lines observed in the 500—700 cm^{-1} region were assigned to the C–Se stretching vibrations. Correlations of the C–Se stretching frequencies to the molecular conformations were found.

Recently, the rotational isomers about the C–Se bond have been confirmed in our laboratory to exist in ethyl methyl selenide and isopropyl methyl selenide.[1] For dialkyl disulfides[2] and dialkyl sulfides[3] of a homologous series, useful correlations of the C–S stretching frequencies to the molecular conformations about the C–C bonds adjacent to the C–S bond have been found, similar to the C–Cl stretching frequencies of alkyl chlorides.[4]

In the present note, therefore, we will study the C–Se stretching frequencies of dialkyl selenides in relation to their molecular conformations.

Results and Discussion

The Raman spectra of dimethyl selenide, ethyl methyl selenide, isopropyl methyl selenide, diethyl selenide, methyl propyl selenide, and *s*-butyl methyl selenide are measured in the liquid and solid states. For these selenides, the C–Se stretching vibrations are expected in the region of 600 cm^{-1} on the basis of the assignments of dimethyl selenide.[5] The most intense Raman lines assigned to the C–Se stretching vibrations are observed in the 500—700 cm^{-1} region; the other vibrations are not expected in this region. Figure 1 shows the liquid and solid spectra in this region, together with the results of the corresponding dialkyl sulfides.[6–8] Although only two Raman lines are expected for one isomer, too many Raman lines are observed in the liquid state for these selenides except for dimethyl selenide. Rotational isomers, therefore, coexist in the liquid state, and only one isomer persists in the solid state. For ethyl methyl selenide, isopropyl methyl selenide, and diethyl selenide, the patterns of the spectral changes from the liquid to the solid states are the same as those of the sulfides. It is estimated that the *gauche* (G) form for ethyl methyl selenide, the molecular form with the C_1 symmetry for isopropyl methyl selenide, and the TT form for diethyl selenide persist in the solid state, in analogy with the cases of the corresponding sulfides.[6–8] For methyl propyl selenide, the CH_3–Se stretching vibrations of all the isomers may be assigned to the Raman line at 591 cm^{-1}. The CH_3–Se stretching vibration is considered to be less affected by a residual part of a molecule, because the frequency difference between the C–Se stretching vibrations of dimethyl selenide (14 cm^{-1}) is considerably smaller than that of dimethyl sulfide (53 cm^{-1})[5] and for methyl propyl selenide the Raman intensity at 591 cm^{-1} is relatively strong, in comparison with that of methyl propyl sulfides.[9] For methyl propyl selenide, by analogy with the case of methyl propyl sulfide pre-

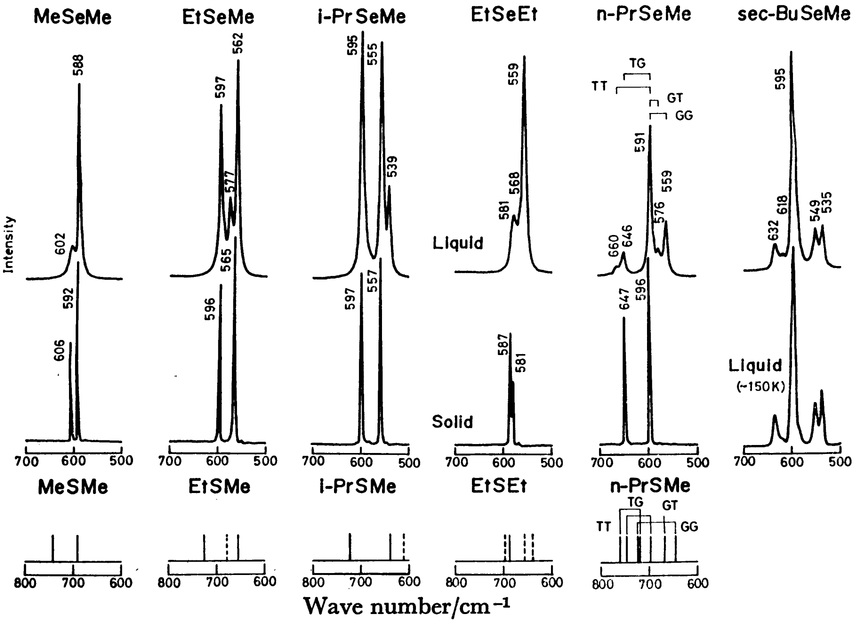

Fig. 1. The Raman spectra of the C–Se stretching vibrations of the dialkyl selenides in the liquid and solid states, together with the results of the dialkyl sulfides. Solid and dotted lines indicate the Raman lines persisting and disappearing in the solid state respectively.

TABLE 1. CHARACTERISTIC C–Se STRETCHING FREQUENCIES (cm^{-1}) OF DIALKYL SELENIDES

Molecules	ν (CH_3–Se)	ν (–CH_2–Se)				ν (>CH–Se)				ν ($\geqslant$C–Se)
		P_H–P_H	P_H–P_C	P_C–P_H	P_C–P_C	S_{HH}–P_H	S_{HH}–P_C	S_{CH}–P_H	S_{CH}–P_C	T_{HHH}
CH_3SeCH_3	588*, 602*	—	—	—	—	—	—	—	—	—
$CH_3SeCH_2CH_3$	597*	562*	577	—	—	—	—	—	—	—
$(CH_3CH_2)_2Se$	—	559, 568	581*	—	—	—	—	—	—	—
$CH_3SeCH_2CH_2CH_3$	591*	559	576	646*	660	—	—	—	—	—
$CH_3SeCH(CH_3)_2$	595*	—	—	—	—	539	555*	—	—	—
$CH_3SeCH(CH_3)CH_2CH_3$	595	—	—	—	—	535	549	618	632	—
$((CH_3)_3C)_2Se$[12)]	—	—	—	—	—	—	—	—	—	527
	588—602	559—581		646—660		535—555		618—632		527
Alkyl bromides[10)]	611	557—617		635—649		529—588		608—617		506—524

viously investigated in detail,[9)] it is estimated that the TG $(-CH\overset{T}{-}CH\overset{G}{-}Se-)$ form persists in the solid state and that the TT, TG, GT, and GG forms coexist in the liquid state. At present, the solid spectrum of *s*-butyl methyl selenide is not obtained. However, the rotational isomers may coexist in the liquid state, since the changes in the Raman intensities are observed at different temperatures. The most intense Raman line at 595 cm^{-1} may be assigned to the CH_3–Se stretching vibrations of all the isomers, in a manner similar to that used for methyl propyl selenide.

Table 1 summarizes the observed frequencies of the Raman lines due to the C–Se stretching vibrations of the dialkyl selenides in the liquid state; asterisks indicate the Raman lines persisting in the solid state. The P_H, P_C, S_{HH}, S_{CH}, and T_{HHH} values in this table are the same as those used in previous papers.[2,4)] For the notation of the molecular form, the first symbol refers to the internal rotation about the C–C bond adjacent to the C–Se bond, and the second symbol, to that about the C–Se bond. The frequency differences in the C–Se stretching vibrations caused by the conformation about the C–C bond adjacent to the C–Se bond (83—85 cm^{-1}) are larger than those caused by the conformation about the C–Se bond (14—22 cm^{-1}). On the other hand, for the C–S stretching vibrations, the frequency differences about the C–C bond have been reported to be 51—105 cm^{-1}, which are similar in magnitude to those in the case of the selenides; those about the C–S bond are 26—35 cm^{-1}, a little larger than those of the selenides.[2,3)] The characteristic CH_3–Se stretching vibrations are observed in the 588—602 cm^{-1} region of dimethyl selenide. In the case of the primary selenides, the C–Se stretching vibrations due to the P_H and P_C forms about the C–C bond lie in the regions of 559—581 cm^{-1} and 646—660 cm^{-1} respectively. For the secondary selenides, the C–Se stretching vibrations due to the S_{HH} and S_{CH} forms about the C–C bond lie in the regions of 535—555 cm^{-1} and 618—632 cm^{-1} respectively. The observed frequencies for the dialkyl selenides, in general, correspond very well to the C–Br stretching frequencies of alkyl bromides,[10)] much as in the case between dialkyl sulfides and alkyl chlorides.[3)]

Experimental

The samples were prepared according to the methods previously reported[11)] and were purified by fractional distillation. The resulting purities were estimated to be higher than 98%, as confirmed by gas-chromatographic analysis. All the boiling points are uncorrected. CH_3SeCH_3: bp 57 °C (reported bp[11)] 56—57 °C); NMR (CCl_4): δ 1.93 (6H, s, Se $(C\underline{H}_3)_2$). $C_2H_5SeCH_3$: bp 85 °C; NMR (CCl_4): δ 1.37 (3H, t, J=7 Hz, $CH_2C\underline{H}_3$), 1.91 (3H, s, $SeC\underline{H}_3$), 2.48 (2H, q, J=7 Hz, $SeC\underline{H}_2$). $(C_2H_5)_2Se$: bp 108 °C (reported bp[11)] 107—108 °C); NMR (CCl_4): δ 1.38 (6H, t, J=7 Hz, Se $(CH_2C\underline{H}_3)_2$), 2.52 (4H, q, J=7 Hz, Se $(C\underline{H}_2CH_3)_2$). *i*-$C_3H_7SeCH_3$: bp 103 °C; NMR (CCl_4): δ 1.40 (6H, d, J=7 Hz, $CH(C\underline{H}_3)_2$), 1.92 (3H, s, $SeC\underline{H}_3$), 2.96 (1H, quintet, J=7 Hz, $SeC\underline{H}$). $C_3H_7SeCH_3$: bp 113 °C; NMR (CCl_4): δ 0.99 (3H, t, J=7 Hz, $CH_2C\underline{H}_3$), 1.65 (2H, sex, J=7 Hz, $C\underline{H}_2CH_3$), 1.90 (3H, s, $SeC\underline{H}_3$), 2.46 (2H, t, J=7 Hz, $SeC\underline{H}_2$). *s*-$C_4H_9SeCH_3$: bp 128 °C; NMR (CCl_4): δ 0.97 (3H, t, J=7 Hz, $CH_2C\underline{H}_3$), 1.36 (3H, d, J=7 Hz, $CHC\underline{H}_3$), 1.57 (2H, quintet, J=7 Hz, $C\underline{H}_2CH_3$), 1.87 (3H, s, $SeC\underline{H}_3$), 2.75 (1H, sex, J=7 Hz, $SeC\underline{H}$).

The Raman spectra were recorded on a JEOL Raman Spectrometer (Model JRS-400D) with an argon-ion laser. For measurements of the solid spectra, samples in ampoules were held on a copper block cooled with liquid nitrogen in a vacuum.

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