CHEMISTRY LETTERS, pp. 1221-1224, 1976. Published by the Chemical Society of Japan

THE VIBRATIONAL SPECTRA AND ROTATIONAL ISOMERISM OF ETHYL METHYL SELENIDE AND METHYL i-PROPYL SELENIDE

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The vibrational spectra of dimethyl selenide, ethyl methyl selenide, and methyl i-propyl selenide were measured in the gaseous, liquid, and solid states. The rotational isomers about the C-Se bond were confirmed to exist for ethyl methyl selenide and methyl i-propyl selenide.

There are gradual decreases in the barriers to internal rotation in going from dimethyl ether and dimethyl sulfide to dimethyl selenide.1) In ethyl methyl ether2) and sulfide,3) rotational isomers of the trans (T) and gauche (G) forms have been reported to coexist in the gaseous and liquid states. The T form is more stable than the G form by 1.1 kcal/mol for the ether,4) while the G form is more stable than the T form by 0.14 kcal/mol for the sulfide.3) Moreover, the T form only persists in the solid state for the ether,2) but the G form for the sulfide.3)

In this paper, in order to investigate these differences of a homologous series and the behavior of the lower barrier to internal rotation about the C-Se bond, we will study the molecular vibrations of such simple alkyl selenides as dimethyl selenide, ethyl methyl selenide, and methyl i-propyl selenide in relation to their rotational isomerism.

The samples were prepared according to the methods previously reported5) and were purified by fractional distillation. The purities of the samples were checked by NMR and gas chromatography.

The Raman spectra were recorded on a JEOL Raman Spectrometer (Model JRS-400D) with an argon-ion laser. For the measurements on the solid state, the samples in the ampoules were held on a copper block cooled with liquid nitrogen in a vacuum. The infrared spectrum was recorded on a Perkin-Elmer instrument (Model 621). The spectrum in the gaseous state was obtained by using a 1-m gas cell fitted with CsI windows.

Figure 1 shows the Raman spectra of dimethyl selenide in the region below 1000 cm^{-1}. The upper and lower spectra were observed for the liquid state at room temperature and for the solid state at about 150 K respectively. In the solid state, the weak Raman lines at 965, 929, 895, and 858 cm^{-1} are assigned to the CH_3 rocking vibrations, the very strong Raman lines at 606 and 592 cm^{-1} to the C-Se antisymmetric and symmetric stretching vibrations respectively, and the Raman line at 234 cm^{-1} to the CSeC deformation vibration, according to the assignments of the liquid spectrum by Allkins and Hendra.6) The very weak Raman lines at 187 and 176 cm^{-1} may be

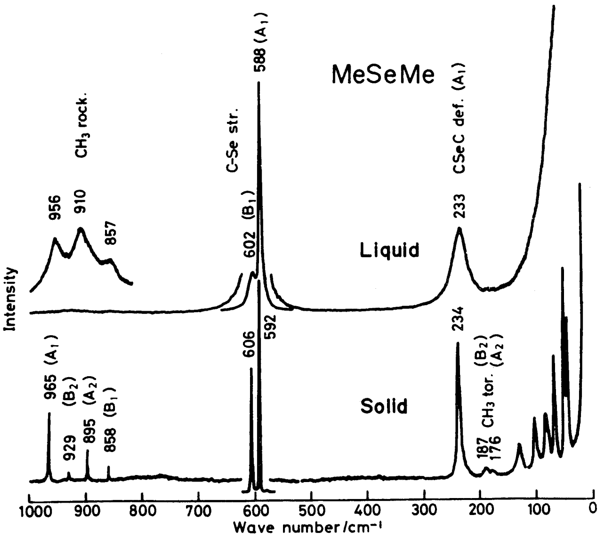

Fig. 1. The Raman spectra of dimethyl selenide. A_1, A_2, B_1, and B_2 indicate the symmetry species of the C_{2v} point group.

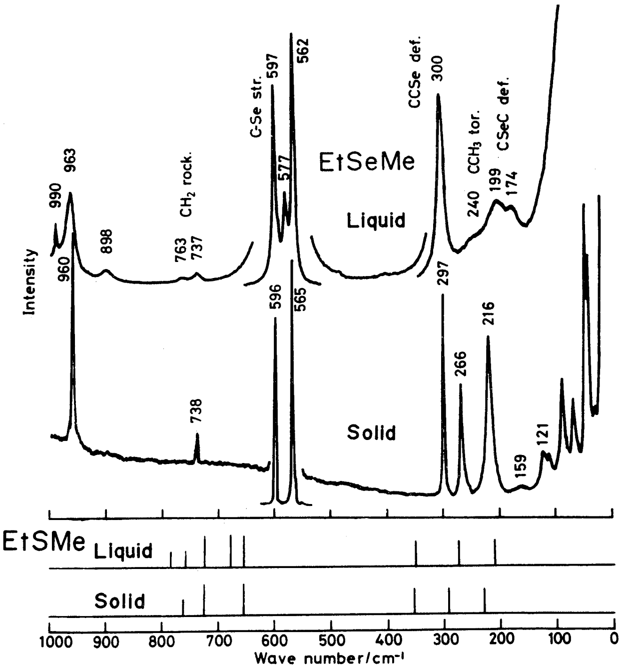

Fig. 2. The Raman spectra of ethyl methyl selenide and ethyl methyl sulfide.

assigned to the CH_3 torsional vibrations (the calculated values by the use of the barrier height, V_3, of 1.5 kcal/mol have been reported to be 163 (B_2) and 160 (A_2) cm^{-1} [7]). The Raman lines below 150 cm^{-1} may be assigned to the lattice vibrations. For dimethyl selenide, the numbers of the Raman lines in the 150-1000 cm^{-1} region indicate the presence of only one isomer both in the liquid and solid states.

Figure 2 shows the Raman spectra of ethyl methyl selenide in the liquid and solid states, together with those of ethyl methyl sulfide.[3] Several Raman lines in the liquid state vanish in the solid state. The pattern of the spectral change from the liquid to solid states in the 150-800 cm^{-1} region is the same as that of the sulfide. In this region, seven fundamental vibrations are expected for each of the T and G forms, including one CH_2 rocking, two C-Se stretching, two skeletal deformation, and two CH_3 torsional vibrations. In the solid state, the weak Raman line at 738 cm^{-1} is assigned to the CH_2 rocking vibration, the very strong Raman lines at 596 and 565 cm^{-1} to the CH_3-Se and CH_2-Se stretching vibrations respectively, indicating the existence of only one isomer. The Raman lines at 763 and 577 cm^{-1} in the liquid state are assigned to the CH_2 rocking and C-Se stretching vibrations of the other isomer respectively. However, in the solid state, three strong Raman lines are observed in the 200-400 cm^{-1} region of the skeletal deformations, though the CH_3 torsional vibrations may in general be very weak in the Raman scattering. It is supposed that the isomer persisting in the solid state is the G form so that the CCH_3 torsional vibration at 266 cm^{-1} is extensively hybridized with the skeletal vibrations at 297 and 216 cm^{-1}, in analogy with the case of ethyl methyl sulfide.[3] The same conclusion for the molecular forms is obtained from the infrared band contours in the gaseous state. The CH_2 rocking bands may have the c-type for the

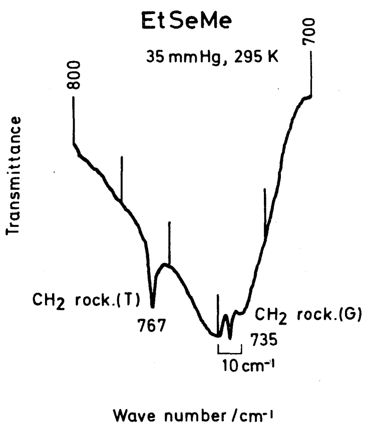

Fig. 3. The infrared band contours of the CH_2 rocking vibrations of ethyl methyl selenide.

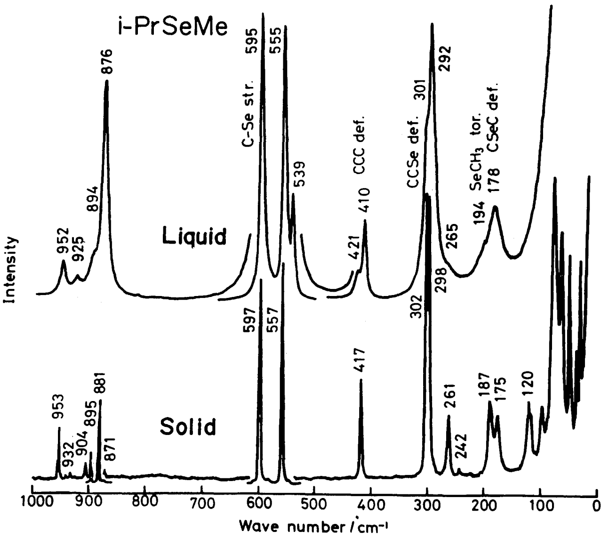

Fig. 4. The Raman spectra of methyl i-propyl selenide.

T form and the ab-type for the G form in the asymmetric top case. The band at 767 cm^{-1} disappearing in the solid state is of the c-type, while the band at 735 cm^{-1} is of the ab-type, as is shown in Fig. 3.

Figure 4 shows the Raman spectra of methyl i-propyl selenide in the liquid and solid states. By comparing the spectra with that of ethyl methyl selenide, the very strong Raman lines at 597 and 557 cm^{-1} in the solid state are assigned to the CH_3-Se and CH-Se stretching vibrations respectively, indicating the existence of only one isomer. The Raman line at 539 cm^{-1} in the liquid state is assigned to the C-Se stretching vibration of any other isomer. Seven fundamental vibrations are expected to lie in the 150-500 cm^{-1} region for each of the isomers, including four skeletal deformation, two CCH_3 torsional, and one $SeCH_3$ torsional vibrations. In this region, too many Raman lines to be expected for the skeletal vibrations of one isomer are observed in the solid state. It is considered that the molecular form with the C_1 symmetry (C_1 form) persists in the solid state so that the skeletal deformation vibrations are extensively hybridized with the CH_3 torsional vibrations, in analogy to the case of ethyl methyl selenide.

In order to confirm the molecular forms of methyl i-propyl selenide, the skeletal vibrations were calculated. The structural parameters used were the bond lengths[1)] r(C-Se)= 1.943 A, r(C-C)= 1.54 A, r(C-H)= 1.093 A, the bond angle of ϕ(CSeC)= 96°11', the tetrahedral angles for the carbon atoms, and the internal rotation angles of 180 and 60°. The CH_3 and CH_2 groups were treated as unit masses. Force constants of the Urey-Bradley type used were transferred from those reported in the literature and some of them were adjusted to predict well the observed frequencies of dimethyl selenide and ethyl methyl selenide.[8)] Table 1 gives the observed and calculated frequencies of the C-Se stretching and skeletal deformation vibrations of dimethyl selenide, ethyl methyl selenide, and methyl i-propyl selenide, together with the predominant potential energy distributions. For methyl i-propyl selenide, the calculation indicates the existence of the C_1 form in the solid state. From the comparison between the observed and calculated frequencies, the Raman lines at 597 cm^{-1} for ethyl methyl selenide and at 595 cm^{-1} for methyl i-propyl selenide can be assigned to the CH_3-Se stretching vibration for each of the isomers, which are negligibly hybridized with another C-Se stretching vibration.

Table 1. The observed and calculated frequencies (cm^{-1}) of alkyl selenides

Obsed	Calcd		P. E. D.
MeSeMe			
602	607		$\nu_a CH_3$-Se
588	580		$\nu_s CH_3$-Se
233	231		δCSeC
EtSeMe	T form	G form	
597	598	602	νCH_3-Se
577	573		νCH_2-Se
562		566	νCH_2-Se
300	292	298	δCCSe
199		216	δCSeC
174	186		δCSeC

Obsed	Calcd		P. E. D.
i-PrSeMe	C_s form	C_1 form	
595	605	596	νCH_3-Se
555		561	νCH-Se
539	557		νCH-Se
421	417		δCCC
410		411	δCCC
301		306	δ_aCCSe
292	297		δ_aCCSe
265	270	260	δ_sCCSe
178	166	174	δCSeC

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8) S. Mizushima and T. Shimanouchi, Infrared Absorption and the Raman Effect, Kyoritsu, Tokyo, 1958; H. Sugeta, *Spectrochim. Acta*, 31A, 1729 (1975); K(C-H)= 4.30, K(CH_3-CH_2)= 4.00, K(CH_3-C)= 3.40, H(C-C-C)= 0.250, H(C-C-H)= 0.250, H(Se-C-H)= 0.180, F(C·C·C)= 0.200, F(C·C·H)= 0.500, F(Se·C·H)= 0.390 md./A, and κ(CH_2)= 0.029 md.A; K(CH_3-Se)= 2.60, K(CH_2-Se)= 2.10, K(C-Se)= 0.80, H(C-C-Se) = 0.190, H(C-Se-C)= 0.170, F(C·C·Se)= 0.290, F(C·Se·C)= 0.060, P(C-Se)= -0.110 md./A, and Y(C-Se)= 0.047 md.A.

(Received September 20, 1976)