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Microwave Spectrum, Barrier to Internal Rotation, and Dipole Moment of Methyl Selenocyanate

Takeshi SAKAIZUMI,* Yoshio KOHRI, Osamu OHASHI, and Ichiro YAMAGUCHI
Department of Chemistry, Faculty of Science and Technology, Sophia University, Kioi-cho, Chiyoda-ku, Tokyo 102

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Microwave rotational spectra of five isotopic species of methyl selenocyanate (CH_3SeCN with ^{82}Se, ^{80}Se, ^{78}Se, ^{77}Se, and ^{76}Se) in the ground vibrational state, and two isotopic species of methyl selenocyanate-d_3 (CD_3SeCN with ^{80}Se and ^{78}Se) in the ground and first excited states of the methyl torsional mode have been assigned in the 8.0 to 35.5 GHz frequency range. For the most abundant species in the ground vibrational state, the rotational constants determined are $A_A=10147\pm2$, $B_A=3483.57\pm0.04$, and $C=2631.58\pm0.04$ MHz for $CH_3{}^{80}SeCN$ and $A=8322.57\pm0.81$, $B=3308.06\pm0.02$, and $C=2436.92\pm0.01$ MHz for $CD_3{}^{80}SeCN$. The A-E splittings due to the methyl internal rotation were observed for the rotational transitions in the ground vibrational state for the normal species and in the first excited state of the methyl torsional mode for the deuterated species. Analysis of the splittings gave a barrier height to the methyl internal rotation of 1241 ± 50 and 1228 ± 50 cal/mol for the CH_3 and CD_3 species, respectively. Stark measurements yielded the principal axis dipole moments of $\mu_a=4.35\pm0.04$, $\mu_b=0.76\pm0.10$, and the total dipole moment of $\mu=4.42\pm0.05$ D for $CH_3{}^{80}SeCN$, and $\mu_a=4.31\pm0.04$, $\mu_b=0.67\pm0.07$, and $\mu=4.36\pm0.04$ D for $CD_3{}^{80}SeCN$. The direction of the dipole moment in the molecule is discussed.

The microwave spectra of alkyl compounds having an isocyanato (–N=C=O) or an isothiocyanato (–N=C=S) group have been studied: ethyl isocyanate (CH_3CH_2NCO)[1)] and ethyl isothiocyanate (CH_3CH_2NCS).[2)] There have been several studies of the microwave spectra of molecules having a C–Se bond which is an axis of internal rotation, *e.g.*, CH_3SeH[3)] and $(CH_3)_2Se$.[4)]

Studies of the microwave spectra of a series of compounds, CH_3SeH,[3)] CH_3SH,[5)] and CH_3OH,[6)] have been made. Among the series, methane selenol had the lowest potential barrier hindering the methyl internal rotation and the longest bond which is the internal rotation axis (see Table 13). The potential barrier of methanethiol is higher than that of methanol, while the C–S bond in methanethiol is longer than the C–O bond in methanol. There seems no simple parallelism between the height of the potential barrier and the bond length for this series, but for a series of dimethyl compounds, $(CH_3)_2Se$,[4)] $(CH_3)_2S$,[7)] and $(CH_3)_2O$,[8)] it does exist as shown in Table 13.

Therefore, it is of interest to study the potential barrier of methyl selenocyanate and to compare it with those of the related compounds in relation to the bond length. In this paper, the spectrum of methyl selenocyanate will be reported, and the barrier height and dipole moment will be discussed.

Experimental

Methyl selenocyanate was prepared by mixing methyl iodide with a cold solution of potassium selenocyanate in ethanol.[9)] An exothermic reaction occurred immediately after adding the iodide followed by the deposition of potassium halides. The mixture was mildly refluxed for 4 h after standing for 30 min at room temperature. The solvent was removed by distillation in a stream of nitrogen and the resultant slurry steam-distilled, giving crude yellow methyl selenocyanate (40 to 50% yield). Reduced pressure distillation with a nitrogen leak yielded a pale yellow product. Methyl selenocyanate-d_3 (CD_3SeCN) was prepared by reacting 99% enriched CD_3I(E. Merk Co., Ltd.) with KSeCN according to the method of normal species. The normal species was identified by the IR and proton NMR spectra, while the deuterated one only by the IR.

The rotational spectra were obtained in the frequency region from 8.0 to 35.5 GHz with a conventional 100-kHz squares-wave Stark modulation spectrometer. The waveguide was cooled with Dry Ice. Transition frequencies were measured with a Hewlett-Packard Model 5245L electronic counter with a 5257A transfer oscillator.

Results and Discussion

Assignment of Spectrum of CH_3SeCN. A model of the molecular structure was constructed based upon the following known molecular parameters: methyl group and C–N bond in CH_3SCN,[10)] Se–CH_3 bond in CH_3SeH,[3)] Se–CN bond in selenophene,[11)] and angle C–Se–C in dimethyl selenide.[4)] The assumed structural parameters are listed in Table 1. The assumed molecular structure and bond moment considerations indicated that the CH_3SeCN molecule should be an asymmetric prolate rotor ($\kappa=-0.77$) with a large component of the dipole moment lying along the a-principal axis. A search for the a-type R-branch transitions, $3_{13}\leftarrow2_{12}$, $3_{03}\leftarrow2_{02}$, and $3_{12}\leftarrow2_{11}$, in the predicted frequency range was fruitful. The transitions of the K-doublet ($K_{-1}=1$ and 2) on the higher frequency side with respect to the $K_{-1}=0$ line split into A and E components due to the hindered internal rotation of the methyl group. A characteristic A-E splitting of the $J=4\leftarrow3$ transition with $K_{-1}=3$ was observed for $CH_3{}^{80}SeCN$ as shown in Fig. 1. The assignments of the lines for the isotopic species (^{82}Se, ^{80}Se, ^{78}Se, ^{77}Se, and ^{76}Se) were made

TABLE 1. ASSUMED STRUCTURAL PARAMETERS

	Length(Å)		Angle(°)
C–H :	1.093[a)]	H–C–H :	109.4[a)]
C≡N :	1.156[a)]	H–C–Se :	109.6[a)]
C–Se :	1.958[b)]	C–Se–C :	97.06[d)]
Se–CN :	1.832[c)]	Se–C≡N :	180

a) Ref. 10. b) Ref. 3. c) Ref. 11. d) Ref. 4.

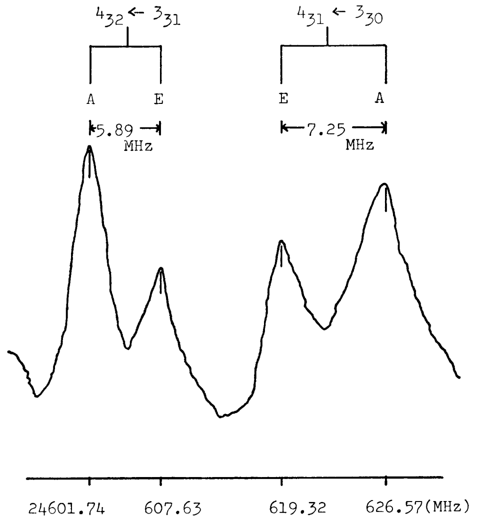

Fig. 1. Observed spectrum of $4_{32}\leftarrow 3_{31}$ and $4_{31}\leftarrow 3_{30}$ transitions in $CH_3{}^{80}SeCN$ showing their characteristic A-E splitting.

based on the Stark effects and the relative intensities corresponding to the natural abundances (9.1, 49.8, 23.5, 7.5, and 9.0%, respectively). The observed and calculated frequencies are in good agreement for transitions up to $J=5\leftarrow 4$ of CH_3SeCN in the ground vibrational state as shown in Table 2. The rotational constants in the ground vibrational state of the A-species were obtained by the least-squares method and are listed in Table 3. Almost a constant value of $\Delta I(=I_c-I_b-I_a)$ was obtained for the ^{82}Se, ^{80}Se, ^{78}Se, ^{77}Se, and ^{76}Se isotopic species as shown in Table 3, indicating that the selenium atom is in the molecular symmetry plane as expected. The constant ΔI value also ensures the assignment of the transition lines.

The observed values of ΔI, -2.83 to -2.85 amu Å^2, are smaller than the values, -3.12 to -3.26 amu Å^2, usually obtained for molecules with a planar framework and a methyl group whose axis of symmetry lies in the plane.

Deuterated Species. The assignment of the spectrum for the ^{80}Se species was made by the same procedure as for the normal species. The absorption lines due to the excited state of the ^{80}Se species were found in the vicinity of the ground state as shown by the broken lines in Fig. 2. The assignment for the ^{78}Se species was made bearing in mind the Stark effects and the isotopic shifts

TABLE 2. OBSERVED TRANSITION FREQUENCIES OF METHYL SELENOCYANATE (A-species) (MHz)

Transition	$CH_3{}^{82}SeCN$		$CH_3{}^{80}SeCN$		$CH_3{}^{78}SeCN$		$CH_3{}^{77}SeCN$		$CH_3{}^{76}SeCN$	
	Obsd	$\Delta\nu$	Obsd	$\Delta\nu$	Obsd	$\Delta\nu$	Obsd	$\Delta\nu$	Obsd	$\Delta\nu$
$2_{12}\leftarrow 1_{11}$	11344.57	0.25	11378.56	0.20	11414.04	0.27	—	—	11449.95	−0.49
$2_{02}\leftarrow 1_{01}$	12118.59	−0.48	12153.57	−0.16	12189.47	−0.22	12207.79	−0.29	12226.85	−0.20
$2_{11}\leftarrow 1_{10}$	—	—	13082.20	−0.11	13117.69	−0.19	13136.31	0.07	13154.17a)	−0.82
$3_{13}\leftarrow 2_{12}$	16970.81	0.46	17021.91	0.29	17075.29	0.26	17102.12	0.05	17130.53	0.23
$3_{03}\leftarrow 2_{02}$	17989.90	−0.29	18043.21	0.06	18098.25	0.07	18126.14	−0.18	18155.80	0.47
$3_{22}\leftarrow 2_{21}$	18294.60	0.49	18345.58	0.08	18399.00	0.26	—	—	—	—
$3_{21}\leftarrow 2_{20}$	18597.79	−0.22	18647.65	−0.19	18699.24	−0.05	18726.40a)	0.83	18752.82	0.01
$3_{12}\leftarrow 2_{11}$	19521.58	0.34	19573.37	0.11	19626.88	−0.04	19654.50	−0.11	19682.57	0.34
$4_{14}\leftarrow 3_{13}$	22546.97	0.07	22615.80	0.16	22687.33	0.05	22723.24	−0.30	22761.63	0.22
$4_{04}\leftarrow 3_{03}$	23657.13	−0.14	23729.34	0.02	23804.29	−0.07	23843.17	0.40	23881.99	−0.25
$4_{23}\leftarrow 3_{22}$	24331.79	0.34	24400.77	−0.19	24472.24	−0.08	24508.97	0.17	24545.93a)	−0.53
$4_{32}\leftarrow 3_{31}$	24534.59a)	0.71	24601.74	0.03	24671.14a)	0.64	24709.16a)	1.38	24745.37a)	0.48
$4_{31}\leftarrow 3_{30}$	24557.26a)	−2.71	24626.57a)	−0.95	24695.26a)	−1.79	24731.32a)	−1.79	24768.57a)	−1.49
$4_{22}\leftarrow 3_{21}$	25066.45	−0.34	25131.99	−0.11	25199.01	−0.39	25233.35	−0.41	25269.64	0.18
$4_{13}\leftarrow 3_{12}$	25927.86	0.04	25998.11	0.33	26069.97	−0.03	26107.06	−0.22	26145.76	0.42
$5_{15}\leftarrow 4_{14}$	28066.48	−0.05	28152.89	−0.03	28242.87	−0.17	28288.78	0.11	28336.11	−0.15
$5_{05}\leftarrow 4_{04}$	29109.70	0.13	29200.83	−0.20	29296.70	0.18	29345.50	0.14	29395.70	0.16
$5_{24}\leftarrow 4_{23}$	30318.92	−0.26	30405.52	−0.20	30495.37	−0.13	30541.28	−0.11	30588.43	−0.33
$5_{23}\leftarrow 4_{22}$	31698.27	0.11	31778.89	−0.01	31862.22	0.25	31904.82	0.44	31948.30	−0.15
$5_{14}\leftarrow 4_{13}$	32235.14	0.13	32323.58	0.04	32415.27	0.20	32462.41	0.08	32510.66	0.16

$\Delta\nu=\nu_{obsd}-\nu_{calcd}$. a) Not used for the least-squares fit.

TABLE 3. ROTATIONAL CONSTANTS (MHz) AND MOMENTS OF INERTIA (amu Å^2)a)

	$CH_3{}^{82}SeCN$	$CH_3{}^{80}SeCN$	$CH_3{}^{78}SeCN$	$CH_3{}^{77}SeCN$	$CH_3{}^{76}SeCN$
A_A	10096 ±4	10146 ±2	10199 ±3	10230 ±4	10257 ±4
B_A	3474.89±0.08	3483.57±0.04	3492.48±0.06	3497.12±0.07	3501.81±0.09
C	2623.14±0.08	2631.58±0.04	2640.42±0.06	2644.85±0.07	2649.53±0.08
I_a^A	50.057	49.809	49.547	49.396	49.269
I_b^A	145.436	145.074	144.704	144.512	144.318
I_c	192.660	192.042	191.399	191.079	190.741
ΔI	−2.832	−2.840	−2.851	−2.828	−2.846

a) Conversion factor: 505376 MHz amu Å^2, ΔI(amu Å^2)$=I_c-I_b-I_a$.

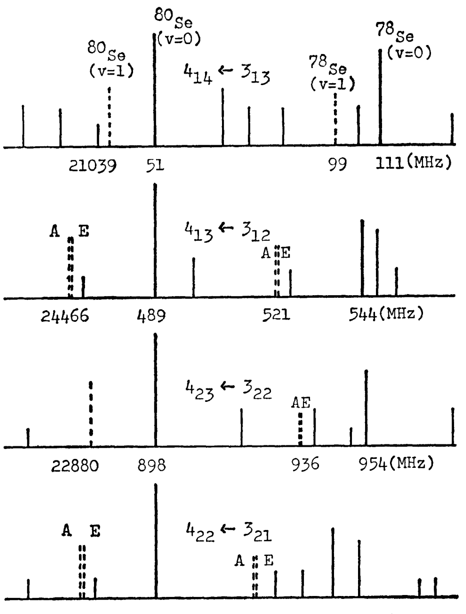

Fig. 2. Observed spectrum of $J=4\leftarrow 3$ transitions in CD_3SeCN.

of the lines predicted from the model. In this spectrum the strong satellite lines due to the vibrationally excited state appeared in the vicinity of the ground state line. The observed lines for the excited state of the ^{78}Se species are also shown by the broken lines in Fig. 2. The broken lines were assigned to the first excited state of the methyl torsional mode because of the splitting of the A-E doublet. The observed and calculated frequencies for CD_3SeCN in the ground and first excited vibrational states of the A-species are in good agreement as given in Table 4. The rotational constants in the ground and excited states of the A-species are listed in Table 5.

r_s(H⋯H) Distance. The distance between the out-of-plane H atoms was determined from the moments of inertia for the normal and deuterated species. The distance between the H atoms is related to the effective moments of inertia as follows,

$$I_a^\circ + I_b^\circ - I_c^\circ = m_H r_e^2 - \Delta_c, \tag{1}$$

where r_e is the equilibrium distance between the two out-of-plane H atoms. The major contribution to Δ_c arises from the low-frequency in-plane motions of the heavy atom skeleton[12] and hence the effect of isotopic substitution of the out-of-plane hydrogen atoms on Δ_c should be small. The contribution of the in-plane vibration may be estimated by using the following approximate equation,[12]

$$\Delta_c = 4K/\omega, \tag{2}$$

where ω is the frequency of the lowest in-plane vibration in cm^{-1} and $K=h/8\pi^2=16.863$ amu Å^2 cm^{-1}. Equation 2 is given for planar molecules, but it is suitable for such cases as non-planar molecules (X_2YZ_2 and CH_3CXO) with a heavy planar skeleton.[12] Substitution of the infrared data for the C–Se–C bending mode ($\omega=166$ cm^{-1})[13] into Eq. 2 gives $\Delta_c=0.406$ amu Å^2. Using Eqs. 1 and 2 for ^{80}Se and ^{78}Se species the values of r_e(H⋯H) and r_e(D⋯D) obtained are listed in Table 6.

The change in the moments of inertia from the normal to the deuterated species gives the following relation,

TABLE 4. OBSERVED FREQUENCIES OF METHYL SELENOCYANATE-d_3 (MHz)

Transition	$CD_3{}^{80}SeCN$				$CD_3{}^{78}SeCN$			
	(v=0)		(v=1)		(v=0)		(v=1)	
	Obsd	$\Delta\nu$	Obsd	$\Delta\nu$	Obsd	$\Delta\nu$	Obsd	$\Delta\nu$
$3_{13}\leftarrow 2_{12}$	15866.83	0.08	15857.27	0.21	15911.01	−0.38	15902.06	0.29
$3_{03}\leftarrow 2_{02}$	16828.84	0.18	16816.53	0.28	16875.04	0.24	16862.49	0.23
$3_{22}\leftarrow 2_{21}$	17235.14	0.18	17221.05	0.38	17276.66	0.17	17261.97	−0.12
$3_{21}\leftarrow 2_{20}$	17641.04	−0.22	17625.38	0.14	17678.14	−0.02	17661.85	−0.08
$3_{12}\leftarrow 2_{11}$	18472.66	0.30	18454.22	0.21	18512.17	−0.13	18493.85	0.08
$4_{14}\leftarrow 3_{13}$	21050.96	−0.24	21039.10	0.11	21111.83	0.01	21099.58	0.14
$4_{04}\leftarrow 3_{03}$	22018.99	0.10	22003.87	−0.23	22084.48	0.23	22069.43	0.12
$4_{23}\leftarrow 3_{22}$	22898.96	0.14	22880.30	0.07	22955.03	−0.11	22936.43	0.09
$4_{22}\leftarrow 3_{21}$	23859.47	0.08	23836.72	0.09	23906.00	0.26	23882.93	0.24
$4_{13}\leftarrow 3_{12}$	24489.53	0.23	24465.73	0.24	24544.66	0.23	24520.39	0.01
$5_{15}\leftarrow 4_{14}$	26166.45	0.08	26151.80	0.07	26243.60	0.13	26228.46	−0.15
$5_{05}\leftarrow 4_{04}$	26981.59	0.02	26965.04	−0.11	27066.38	0.02	27049.92	0.13
$5_{24}\leftarrow 4_{23}$	28494.17	−0.06	28471.54	−0.03	28566.28	0.12	28543.09	−0.14
$5_{23}\leftarrow 4_{22}$	30233.47	−0.26	30203.59	−0.21	30290.03	−0.15	30259.80	−0.08
$5_{14}\leftarrow 4_{13}$	30362.72	0.02	30334.08	−0.03	30435.20	0.12	30405.84	−0.36
$6_{16}\leftarrow 5_{15}$	31215.53	0.02	31198.76	0.08	31309.43	0.03	31291.93	−0.39
$6_{06}\leftarrow 5_{05}$	31809.11	−0.01	31791.45	0.10	31911.62	−0.08	31893.76	0.02
$6_{25}\leftarrow 5_{24}$	34006.48	−0.32	33979.83	−0.60	34094.70	−0.52	34068.82	0.26
$5_{14}\leftarrow 5_{15}$	12853.76	0.30	12810.06	−0.11				
$6_{15}\leftarrow 6_{16}$	17671.20	0.02	17612.15	−0.19				
$7_{16}\leftarrow 7_{17}$	22906.80	−0.20	22832.15	0.14				

$\Delta\nu=\nu_{obsd}-\nu_{calcd}$.

TABLE 5. ROTATIONAL CONSTANTS (MHz) AND MOMENTS OF INERTIA (amu Å^2)

	$CD_3{}^{80}SeCN$		$CD_3{}^{78}SeCN$	
	(v=0)	(v=1)[a]	(v=0)	(v=1)[a]
A	8322.31±0.81	8307.45±0.98	8374.37±1.08	8359.77±1.85
B	3308.06±0.02	3304.21±0.02	3314.17±0.02	3310.28±0.05
C	2436.92±0.01	2436.03±0.02	2444.65±0.02	2443.74±0.04
I_a	60.725	60.834	60.348	60.453
I_b	152.771	152.949	152.489	152.669
I_c	207.383	207.459	206.727	206.804
ΔI	−6.113	−6.324	−6.110	−6.317

a) A-species, ΔI(amu Å^2)$=I_c-I_b-I_a$.

$$\Delta I_a^\circ + \Delta I_b^\circ - \Delta I_c^\circ = (m_D - m_H) r_s^2, \tag{3}$$

where $\Delta I_a^\circ = I_a^\circ(CD_3) - I_a^\circ(CH_3)$, *etc.* In Eq. 3, the vibrational effect is effectively cancelled if $\varDelta_c$ is the same for the CH_3 and CD_3 isotopic species.[14] The values of r_s obtained using Eq. 3 for ^{80}Se and ^{78}Se species are listed in Table 6.

TABLE 6. NONBONDED H···H DISTANCE (Å) IN METHYL GROUP

	$CH_3{}^{80}SeCN$	$CH_3{}^{78}SeCN$
r_s	1.802±0.009	1.798±0.012
r_e(D–D)	1.799±0.001	1.798±0.001
r_e(H–H)	1.795±0.004	1.799±0.006

TABEL 7. COMPARISON OF THE H···H DISTANCE (Å)

Molecule	r_s
CH_3SeCN	1.800[a]
CH_3CHO	1.776[b]
CH_3CFO	1.770[b]
CH_3CClO	1.768[b]
CH_3COOH	1.774[b]
CH_3COCN	1.766[b]

a) This work. b) Ref. 14.

Table 7 shows a comparison of the H···H distance in some related molecules. The r_s in CH_3SeCN obtained in this work is larger than that in the other molecules.

The Bond Length $r_{Se-C(methyl)}$. The r_s-coordinate of the carbon atom in the methyl group could not be determined, because the spectrum of the $^{13}CH_3$ species was not observed. However the bond length r_{Se-C} may be obtained using the moments of inertia of the four isotopic species ($CH_3{}^{80}SeCN$, $CH_3{}^{78}SeCN$, $CD_3{}^{80}SeCN$, and $CD_3{}^{78}SeCN$). If the methyl group is assumed to have C_{3v} symmetry, r_{Se-C} is expressed by the relation (see Appendix),

$$r_{Se-C} = \sqrt{1/3}\,r_{C-H}[\sqrt{\cos\theta - 1 + (Z/r_{C-H}^2)} \\ - \sqrt{2\cos\theta + 1}], \tag{4}$$

where θ and r_{C-H} are the angle H–C–H and the C–H bond length in the methyl group and Z is a quantity calculated from the observed moments of inertia (I_c) of the four isotopic species and their molecular weights. Assuming r_{C-H} to be 1.085 Å as in the case of the CH_3SeH molecule, the H–C–H angle θ may be obtained as 112° from the r_s(H···H) distance determined (Table 6). With these values, the bond distance, r_{Se-C}, may be estimated from Eq. 4 to be 1.950 Å. The error in r_{Se-C} depends on the estimation of r_{C-H} distance. If the estimation error of r_{C-H} is ±0.008 Å, the error of r_{Se-C} is ±0.025 Å.

The remaining parameters, $r_{C\equiv N}$, r_{Se-CN}, and the angle C–Se–C, have been fitted to all the observed moments of inertia (except for I_a in normal species). The obtained structural parameters are listed in Table 8 and the observed and calculated moments of inertia are shown in Table 9.

TABLE 8. STRUCTURAL PARAMETERS

Lengh(Å)	Angle(°)
C≡N: 1.160	H–C–H: 112.0
Se–CN: 1.851	C–Se–C: 95.57
C–Se: 1.950	Se–C≡N: 180(assumed)
C–H: 1.085(assumed)	

TABLE 9. THE OBSERVED AND CALCULATED MOMENTS OF INERTIA (amu Å^2)

		Obsd	Calcd	$\varDelta$
$CH_3{}^{82}SeCN$	I_a	50.057	50.086	−0.029
	I_b	145.436	145.820	−0.384
	I_c	192.660	192.645	0.015
$CH_3{}^{80}SeCN$	I_a	49.809	49.836	−0.027
	I_b	145.074	145.439	−0.365
	I_c	192.042	192.013	0.029
$CH_3{}^{78}SeCN$	I_a	49.547	49.575	−0.028
	I_b	144.704	145.047	−0.343
	I_c	191.399	191.361	0.038
$CH_3{}^{77}SeCN$	I_a	49.396	49.441	−0.045
	I_b	144.512	144.848	−0.336
	I_c	191.079	191.028	0.051
$CH_3{}^{76}SeCN$	I_a	49.269	49.304	−0.035
	I_b	144.318	144.645	−0.327
	I_c	190.741	190.688	0.053
$CD_3{}^{80}SeCN$	I_a	60.725	60.705	0.020
	I_b	152.771	152.745	0.026
	I_c	207.383	206.932	0.451
$CD_3{}^{78}SeCN$	I_a	60.348	60.336	0.012
	I_b	152.489	152.443	0.046
	I_c	206.727	206.261	0.466

$\varDelta$=Obsd−Calcd.

Table 10. Internal rotation splitting (MHz) of methyl selenocyanate

Transition	$CH_3{}^{82}SeCN$		$CH_3{}^{80}SeCN$		$CH_3{}^{78}SeCN$		$CH_3{}^{77}SeCN$		$CH_3{}^{76}SeCN$	
	Obsd	$\Delta\nu$[a]	Obsd	$\Delta\nu$[a]	Obsd	$\Delta\nu$[a]	Obsd	$\Delta\nu$[a]	Obsd	$\Delta\nu$[a]
$3_{21}\leftarrow 2_{20}$	1.31	−0.38	1.70	0.15	1.63	−0.09	1.44	−0.26	—	—
$4_{22}\leftarrow 3_{21}$	—	—	0.95	−0.19	1.08	−0.14	—	—	1.15	−0.08
$4_{31}\leftarrow 3_{30}$	—	—	7.25	−0.06	7.81	0.18	7.86	0.30	7.81	0.14
$4_{32}\leftarrow 3_{31}$	−6.34	−0.41	−5.89	−0.17	−5.99	−0.04	−5.72	0.19	−5.89	0.09
$4_{13}\leftarrow 3_{12}$	0.96	0.14	1.04	0.01	0.95	−0.14	1.03	−0.04	1.08	−0.01
$5_{23}\leftarrow 4_{22}$	1.37	−0.13	1.31	−0.09	1.38	−0.10	1.43	−0.03	1.27	−0.22
$5_{24}\leftarrow 4_{23}$	0.52	−0.33	0.57	−0.23	0.61	−0.24	0.59	−0.24	0.63	−0.22
$5_{14}\leftarrow 4_{13}$	1.34	0.05	1.10	−0.11	1.14	−0.14	1.31	0.05	1.44	0.15

a) $\Delta\nu = (\nu_A - \nu_E)_{obsd} - (\nu_A - \nu_E)_{calcd}$.

Table 11. Internal rotation splitting (MHz) of methyl selenocyanate-d_3

Transition	$CD_3{}^{80}SeCN$ ($v=1$)		$CD_3{}^{78}SeCN$ ($v=1$)	
	Obsd	$\Delta\nu$[a]	Obsd	$\Delta\nu$[a]
$3_{12}\leftarrow 2_{11}$	−1.37	−0.10	−1.25	0.03
$4_{04}\leftarrow 3_{03}$	−0.60	0.01	—	—
$4_{23}\leftarrow 3_{22}$	—	—	−1.20	0.03
$4_{22}\leftarrow 3_{21}$	−1.73	−0.12	−1.43	0.19
$4_{13}\leftarrow 3_{12}$	−1.68	−0.09	−1.65	−0.03
$5_{23}\leftarrow 4_{22}$	−2.19	0.06	−2.02	0.25
$5_{14}\leftarrow 4_{13}$	−1.99	−0.17	−2.33	−0.49
$6_{25}\leftarrow 5_{24}$	−1.57	−0.10	−1.48	−0.01
$5_{14}\leftarrow 5_{15}$	−4.12	0.07		
$6_{15}\leftarrow 6_{16}$	−5.44	0.13		
$7_{16}\leftarrow 7_{17}$	−6.91	−0.04		

a) $\Delta\nu = (\nu_A - \nu_E)_{obsd} - (\nu_A - \nu_E)_{calcd}$.

Barrier to Internal Rotation. The A-E splittings due to internal rotation of the methyl group were measured for each isotopic species and are shown in Tables 10 and 11. Analysis of the A-E splittings was achieved using the principal axis method (PAM) developed by Herschbach.[15] The Hamiltonians used in this analysis contained perturbation terms up to second order for A-species and up to third order for E-species. The values of the perturbation coefficients, $W_{v\sigma}^{(n)}$ ($v=0$ or 1 and σ=A or E) were taken from Hayashi and Pierce.[16] The assignment of the E-species transitions was made with the aid of the internal rotation calculation. The parameters required to compute the A-E splitting of the rotational transitions in the PAM formalism are A, B, C, I_α, λ_a, and s. The rotational constants A, B, and C were fixed to the effective values obtained from the least-squares fit of the A-species lines. Assuming r(C–H)=r(C–D), the value of the moment of intertia of the CH_3 group about its axis of symmetry, I_α, was determined using the following relation:

$$I_\alpha(CH_3) = [m_H/(m_D - m_H)][(I_a + I_b - I_c)_{CD_3} - (I_a + I_b - I_c)_{CH_3}]. \qquad (5)$$

The values of $I_\alpha(CH_3)$ for the two pairs of isotopic species, $CH_3{}^{80}SeCN$-$CD_3{}^{80}SeCN$ and $CH_3{}^{78}SeCN$-CD_3-${}^{78}SeCN$ were determined, independently, using Eq. 5 and found to be in good agreement (within 0.017 amu Å^2). The average value of $I_\alpha(CH_3)$=3.267 amu Å^2 was used in the internal rotation analysis involving the methyl group. The moment of inertia of the deuterated methyl group, $I_\alpha(CD_3)$, was obtained from $I_\alpha(CH_3)$ using the relationship

$$I_\alpha(CD_3) = (m_D/m_H) I_\alpha(CH_3) \qquad (6)$$

based on the assumption that CH_3 and CD_3 groups are identical except for the differing masses of the hydrogen and deuterium atoms. Substitution of the values of $I_\alpha(CH_3)$=3.267 amu Å^2 into Eq. 6 yields $I_\alpha(CD_3)$= 6.529 amu Å^2, which was used in the internal rotation analysis of the methyl selenocyanate-d_3 species. The direction cosine, λ_a($\lambda_a = \cos\varphi$, where φ is the angle between the axis of symmetry of the threefold symmetric top and the a-principal axis), may be obtained from the structural parameters listed in Table 8, assuming that the axis of symmetry of the CH_3 and CD_3 groups coincides with the C–Se bond. From the assigned transitions of the A- and E-species, an approximate value of s, a parameter of the Mathieu equation, could be evaluated. Using the approximate values of s and the internal rotation parameters, the transitions of the E-species were predicted. The E-species lines were observed in the vicinity of the predicted frequencies and consequently were assigned. The observed and calculated A-E splittings of CH_3SeCN and CD_3SeCN are in good agreement as shown in Tables 10 and 11. The s values for the various isotopic species were obtained by the least-squares fit to the observed A-E splittings. The results of the internal rotation analysis are listed in Table 12. The resulting barriers to the methyl internal rotation are 1241±50 and 1228±50 cal/mol for the CH_3 and CD_3 species, respectively.

Table 12. Internal rotation parameters[a] of methyl selenocyanate

	F (GHz)	λ_a	s	V_3 (cal/mol)
$CH_3{}^{82}SeCN$	158.941	0.316087	36.1±1.0	1234
$CH_3{}^{80}SeCN$	158.968	0.319147	36.6±0.4	1251
$CH_3{}^{78}SeCN$	158.996	0.322314	36.3±0.6	1238
$CH_3{}^{77}SeCN$	159.012	0.323935	36.4±0.5	1242
$CH_3{}^{76}SeCN$	159.027	0.325592	36.3±0.4	1239
$CD_3{}^{80}SeCN$	81.638	0.376662	70.1±0.6	1229
$CD_3{}^{78}SeCN$	81.666	0.380020	70.0±1.4	1227

a) $I_\alpha(CH_3)$=3.267amu Å^2; $I_\alpha(CD_3)$=6.529 amu Å^2.

TABLE 13. BARRIER HEIGHTS (cal/mol) ABOUT C–Se, C–S, AND C–O BONDS (Å) IN SOME RELATED MOLECULES

		M=Se	M=S	M=O
CH_3MH	V_3	1001±50[a]	1270±29[b]	1070[c]
	r(C–M)	1.959±0.010[a]	1.819±0.005[b]	1.427±0.007[c]
CH_3MCN	V_3	1241±50[d]	1600±80[e]	
	r(C–M)	1.950[d]	1.818[e]	
CH_3MCH_3	V_3	1500±20[f]	2132±2[g]	2720[h]
	r(C–M)	1.943±0.001[f]	1.802±0.002[g]	1.410±0.003[h]

a) Ref. 3. b) Ref. 5. c) Ref. 6. d) This work. e) Ref. 10. f) Ref. 4. g) Ref. 7. h) Ref. 8.

Table 13 shows a comparison of the potential barrier in some related molecules. In the series of $(CH_3)_2Se$, $(CH_3)_2S$, and $(CH_3)_2O$, the potential barrier becomes higher as the C–M bond length (M=Se, S, and O) becomes shorter. The same trend holds for the series of CH_3SeCN and CH_3SCN. However, this trend does not hold for the series of CH_3SeH, CH_3SH, and CH_3OH.

Inspection of the data in Table 13 revealed a quantitative trend that the replacement of a hydrogen atom of the selenol group in CH_3SeH by a cyano group to make CH_3SeCN results in an increase of the barrier by about 240 cal/mol. This increment is consistent with the same replacement from CH_3SH to CH_3SCN.

TABLE 14. STARK COEFFICIENTS[a] AND DIPOLE MOMENT (D)

Transition	M	$CH_3{}^{80}SeCN$ Obsd	$CH_3{}^{80}SeCN$ Calcd	$CD_3{}^{80}SeCN$ Obsd	$CD_3{}^{80}SeCN$ Calcd
$2_{02} \leftarrow 1_{01}$	0	−11.2	−11.7		
	1	10.3	10.2		
$2_{11} \leftarrow 1_{10}$	0	9.52	9.11		
$3_{03} \leftarrow 2_{02}$	0	−2.04	−2.06	−2.15	−2.16
	1	−0.514	−0.518	−0.559	−0.555
	2	4.06	4.12	4.26	4.25
$3_{12} \leftarrow 2_{11}$	0	−1.19	−1.13	−0.467	−0.469
	1	−5.30	−4.89	−3.95	−4.03
	2	−14.9	−15.9	−13.8	−14.7
μ_a:		4.35±0.04		4.31±0.04	
μ_b:		0.76±0.10		0.67±0.07	
μ_{total}:		4.42±0.05		4.36±0.04	

a) $[MHz/(V/cm)^2] \times 10^{-5}$.

Stark Effect and Dipole Moment. The dipole moments in the ground vibrational state were determined from the Stark coefficients of the $2_{02} \leftarrow 1_{01}$, $2_{11} \leftarrow 1_{10}$, $3_{03} \leftarrow 2_{02}$, and $3_{12} \leftarrow 2_{11}$ transitions for $CH_3{}^{80}SeCN$ and the $3_{03} \leftarrow 2_{02}$ and $3_{12} \leftarrow 2_{11}$ transitions for $CD_3{}^{80}SeCN$. The c-component of the dipole moment was assumed to be zero because of the plane of symmetry of the molecule as discussed above. The electric-field strength in the absorption cell was calibrated using the dipole moment of OCS, 0.71521 D[17] and the results are given in Table 14. The total dipole moment (4.42 D) is larger than the value of 3.91 D obtained from the dielectric measurement.[18] The same trend is noted for methyl thiocyanate, where the dipole moment obtained by the rotational spectrum is 4.03 D[10] while that obtained from the dielectric measurement is 3.59 D.[18] The replacement of the selenol hydrogen atom by a cyano group results in an increase of the dipole moment by about 3.1 D. This increment is consistent with that of 2.5 D found in changing from CH_3SH to CH_3SCN.

The direction of the dipole moment in the molecule was determined using the values of the dipole moment for both the normal and deuterated species. The observed value of γ ($\cos \gamma = \mu_a/\mu_{total}$), the angle between the direction of the dipole moment and the a-principal axis, is 10.2°±2° for the normal species. Therefore, two directions of the dipole moment are possible in the molecule as shown by two broken lines in Fig. 3. The angle between the a-principal axis for the normal species, CH_3SeCN, and for the deuterated species, CD_3SeCN, was calculated to be 3.8° from the structural parameters in Table 8. Two predicted directions, γ, in CD_3SeCN are 14.0 and 6.4°. The angle γ obtained from the observed data for CD_3SeCN is 8.6°. This is consistent with a predicted value 6.4±2° rather than the other one. Taking account of the electronegativities of the elements (or groups) in this molecule, the above discussion leads to the conclusion that the dipole moment of the molecule lies along the thick arrow shown in Fig. 3.

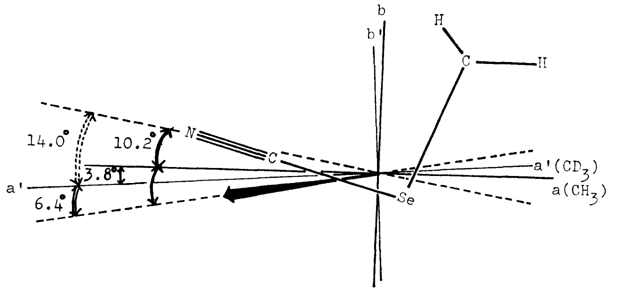

Fig. 3. The direction of dipole moment in methyl selenocyanate.

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Appendix

The molecules studied have a plane of symmetry. If the z axis is chosen as perpendicular to the plane of symmetry, the principal moment of inertia, I_z, is represented by the following equation,

$$I_z = \sum_i m_i r_i^2 - M(X^2+Y^2) \tag{A1}$$

the origin of the coordinate system being taken at an arbitrary point in the molecule, where m_i is the mass of the i-th atom in the normal species and M is the total mass of the molecule. r_i represents the distance of the i-th atom from the origin. X and Y are the coordinates of the center of mass from the origin.

The z axis has been chosen as the principal axis c for the molecules studied in this work. If the selenium atom in the molecule is chosen as the origin of the coordinate system, the moment of inertia, I_c, are given by

$$I = \sum_i m_i r_i^2 - M(X^2+Y^2) \tag{A2}$$

for $CH_3{}^{80}SeCN$ and $CH_3{}^{78}SeCN$ molecules and

$$I = \sum_i m_i r_i^2 - M(X^2+Y^2) + \Delta m(r_4^2+2r_5^2) \tag{A3}$$

for $CD_3{}^{80}SeCN$ and $CD_3{}^{78}SeCN$ molecules, respectively, where the subscript c of I has been eliminated as unnessessary. In Eqs. A2 and A3, the summation is over all atoms in the molecules. r_i's can be identified in Fig. 4. Δm is the difference between the masses of deuterium and hydrogen atoms. The first terms in Eqs. A2 and A3 are identical for molecules with the same Se isotopic species. The coordinates of the center of mass, X and Y, are given by

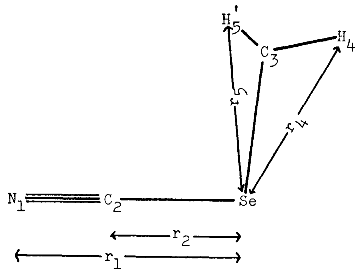

Fig. 4. Model for the calculation of the bond length of $r(Se-CH_3)$.

$$X = \sum_i m_i x_i / \sum_i m_i, \qquad Y = \sum_i m_i y_i / \sum_i m_i \tag{A4}$$

for $CH_3{}^{80}SeCN$ and $CH_3{}^{78}SeCN$, and

$$\left.\begin{aligned} X &= [\textstyle\sum_i m_i x_i + \Delta m(x_4+2x_5)]/(\sum_i m_i + 3\Delta m) \\ Y &= [\textstyle\sum_i m_i y_i + \Delta m(y_4+2y_5)]/(\sum_i m_i + 3\Delta m) \end{aligned}\right\} \tag{A5}$$

for $CD_3{}^{80}SeCN$ and $CD_3{}^{78}SeCN$. x_i and y_i are the coordinates of the i-th atom in the molecule and the summation in Eqs. A4 and A5 is over all the atoms in the molecules. The numerator in Eq. A4 and the first term of the numerator in Eq. A5 are equivalent for the molecules with the same Se isotopic species. From Eqs. A2, A3, A4, and A5, the following relation is obtained,

$$\begin{aligned}(r_4^2+2r_5^2) = {} & [\mu\Delta I_A - \mu'\Delta I_B - (\mu/M_{A'} - \mu'/M_{B'}) \\ & \times (M\Delta I_{AB} + M'\Delta I_{A'B'})]/\Delta m(\mu-\mu'),\end{aligned} \tag{A6}$$

where

$$\begin{aligned} 1/\mu &= 1/M_A + 1/M_{A'}, & 1/\mu' &= 1/M_B + 1/M_{B'}, \\ 1/M &= 1/M_A - 1/M_B, & 1/M' &= 1/M_{A'} - 1/M_{B'}, \\ \Delta I_A &= I_{A'} - I_A, & \Delta I_B &= I_{B'} - I_B \\ \Delta I_{AB} &= I_A - I_B, & \Delta I_{A'B'} &= I_{A'} - I_{B'}. \end{aligned}$$

M_A, $M_{A'}$, M_B, and $M_{B'}$ are the total masses and I_A, $I_{A'}$, I_B, and $I_{B'}$ the principal moments of inertia, I_c, of $CH_3{}^{80}SeCN$, $CD_3{}^{80}SeCN$, $CH_3{}^{78}SeCN$, and $CD_3{}^{78}SeCN$, respectively.

Expressing the right side of Eq. A6 as Z, rewriting the left side in terms of $r_{Se-C(methyl)}$, r_{C-H}, and θ, and assuming that the methyl group has C_{3v} symmetry and the symmetry axis coincides with the Se–C(methyl) bond, then Eq. A6 leads to Eq. 4.

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