A Contribution to the Microwave Spectrum of Dimethyl Selenide *

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The microwave spectra of five isotopic species of dimethyl selenide have been measured and analysed for centrifugal distortion and internal rotation by PAM and IAM.

We investigated the rotational spectra of five isotopic species of dimethyl selenide: $(CH_3)_2{}^nSe$, $n = 76, 77, 78, 80, 82$. The most abundant 78- and 80-isotopic species have been assigned and analysed earlier by Beecher [1]. Our aim was to determine the centrifugal distortion and the hindering potential of internal rotation for comparison between the isotopic species and for a precise prediction of the ground state rotational spectra. We hope hereby to assist the assignment of rotational spectra of torsional excited states currently under investigation for the determination of V_{12}'[2 – 4].

Further we compared the two fundamental methods for the analysis of internal rotation: PAM and IAM [5, 6] which was not yet done for many molecules.

Experimental

The spectra were measured by conventional Stark spectrometers [7, 8] with 33 and 100 kHz modulation frequency. The substance was supplied by Ventron GmbH, Karlsruhe, and used after vacuum distillation.

Analysis and Results

The spectra of the 76-, 77- and 82-isotopic species were assigned with the help of the Stark effect and the similarity of the torsional fine structure after a prediction of the spectra based on the structure [1].

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For the centrifugal distortion analysis the AA-components of the torsion fine structure of the transitions given in Table 1 were used. The analysis was performed with the help of the programs VT 26 and VT 27 written by Typke [9] based on the Hamiltonian of Watson [10].

$$\begin{aligned} H = {} & A P_z^2 + B P_x^2 + C P_y^2 \\ & - \Delta_J P^4 - \Delta_{JK} P^2 P_z^2 - \Delta_K P_z^4 \\ & - \delta_J [P^2 (P_x^2 - P_y^2) + (P_x^2 - P_y^2) P^2] \\ & - \delta_K [P_z^2 (P_x^2 - P_y^2) + (P_x^2 - P_y^2) P_z^2]. \end{aligned} \quad (1)$$

The least square fitted rotational constants, centrifugal distortion parameters and derived parameters together with standard errors are given in Table 2. The highest correlation coefficient is $|\Delta_{JK}, \delta_K| = 0.97$, as can be seen from Table 3.

The rotational constants show the usual change with the isotopic mass. This cannot be stated for the centrifugal distortion constants.

The torsion fine structure was analysed by using the multiplet splittings of Table 1.

The Hamiltonian

$$\begin{aligned} H = {} & A P_z^2 + B P_x^2 + C P_y^2 \\ & + F (p_1 - \mathcal{P}_1)^2 + F (p_2 - \mathcal{P}_2)^2 \\ & + \frac{V_3}{2} (1 - \cos 3\alpha_1) + \frac{V_3}{2} (1 - \cos 3\alpha_2) \\ & + F' \{ (p_1 - \mathcal{P}_1)(p_2 - \mathcal{P}_2) + (p_2 - \mathcal{P}_2)(p_1 - \mathcal{P}_1) \} \end{aligned} \quad (2)$$

without centrifugal distortion terms proved to be sufficient to calculate the torsional splittings. The meaning of the symbols of (2) are given for example in [3].

For the PAM-analysis the Hamiltonian was treated by fourth order van Vleck perturbation theory including denominator correction. A modified program originally written by Rudolph, Schleser and Tan was used. The results are given in Table 4 with V_3 and θ fitted.

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Table 1a—e. Measured transitions of dimethyl selenide for the 76, 77, 78, 80 and 82-Selenium isotopes. The measured frequencies ν_{exp} are given in the order of the symmetry species A_1A_1, EE, A_1E, EA_1. $\Delta\nu_{exp}$ gives the torsional splitting referred to the A_1A_1 component. $\nu_{calc}^{(A_1A_1)}$ was calculated with Hamiltonian (1). $\Delta\nu_{calc}^{(PAM)}$ and $\Delta\nu_{calc}^{(IAM)}$ are the calculated torsional splittings with the deviation $\delta\nu$. All frequencies in MHz.

Transition $J_{K-K+} - J'_{K-'K+'}$	ν_{exp}	$\Delta\nu_{exp}$	$\nu_{calc}^{(A_1A_1)}$ / $\Delta\nu_{calc}^{PAM}$	$\delta\nu$	$\Delta\nu_{calc}^{IAM}$	$\delta\nu$
$(CH_3)_2{}^{76}Se$						
$1_{11} - 0_{00}$	15994.500		15994.440	0.060		
	15993.880	0.620	0.645	-0.025	0.644	-0.024
	15993.250	1.250	1.258	-0.008	1.257	-0.007
	15993.250	1.250	1.322	-0.072	1.320	-0.070
$2_{11} - 2_{02}$	9962.800		9962.834	-0.034		
	9962.021	0.779	0.807	-0.028	0.810	-0.031
	9961.219	1.581	1.617	-0.036	1.630	-0.049
	9961.219	1.581	1.608	-0.027	1.608	-0.027
$2_{21} - 2_{12}$	20673.570		20673.579	-0.009		
	20671.461	2.109	2.088	0.021	2.073	0.036
	20669.796	3.774	3.763	0.011	3.752	0.022
	20669.147	4.423	4.588	-0.165	4.540	-0.117
$2_{12} - 1_{01}$	25097.603		25097.548	0.055		
	25097.023	0.580	0.629	-0.049	0.631	-0.051
	25096.400	1.203	1.246	-0.043	1.252	-0.049
	25096.400	1.203	1.271	-0.068	1.273	-0.070
$2_{21} - 1_{10}$	38879.717		38879.693	0.024		
	38877.685	2.032	2.165	-0.073	2.092	-0.060
	38876.024	3.693	3.758	-0.065	3.747	-0.054
	A		4.662		4.620	
$3_{21} - 3_{12}$	13792.978		13792.973	0.005		
	13791.700	1.278	1.274	0.004	1.270	0.008
	13790.374	2.604	2.622	-0.018	2.621	-0.017
	13790.494	2.484	2.474	0.010	2.470	0.014
$3_{12} - 3_{03}$	15469.834		15469.861	-0.027		
	15468.669	1.165	1.143	0.022	1.150	0.015
	15467.516	2.318	2.290	0.028	2.300	0.018
	15467.516	2.318	2.280	0.038	2.289	0.029
$3_{22} - 3_{13}$	24608.954		24608.943	0.011		
	24606.739	2.215	2.166	0.049	2.161	0.054
	24604.460	4.494	4.250	0.244	4.242	0.252
	24604.460	4.494	4.413	0.081	4.394	0.100
$3_{13} - 2_{02}$	33336.896		33336.995	-0.099		
	33336.390	0.506	0.554	-0.048	0.556	-0.050
	33335.856	1.040	1.099	-0.059	1.111	-0.071
	33335.856	1.040	1.116	-0.076	1.122	-0.082
$4_{22} - 4_{13}$	15345.927		15345.937	-0.010		
	15344.661	1.266	1.274	-0.008	1.278	-0.012
	15343.384	2.543	2.564	-0.021	2.584	-0.041
	15343.384	2.543	2.534	0.009	2.535	0.008
$4_{13} - 4_{04}$	23284.510		23284.513	-0.003		
	23282.820	1.690	1.663	0.027	1.671	0.019
	23281.160	3.350	3.336	0.014	3.342	0.008
	23281.160	3.350	3.317	0.033	3.334	0.016
$4_{32} - 4_{23}$	30605.310		30605.296	0.014		
	30602.235	3.075	3.128	-0.053	3.076	-0.001
	30599.792	5.518	5.552	-0.034	5.535	-0.017
	30598.591	6.719	6.959	-0.240	6.768	-0.049
$4_{31} - 4_{22}$	23371.560		23371.547	0.013		
	23369.500	2.060	2.035	0.025	2.057	0.003
	23366.830	4.730	4.773	-0.043	4.734	-0.004
	23368.060	3.500	3.369	0.131	3.502	-0.002
$4_{23} - 4_{14}$	29861.862		29861.861	0.001		
	29859.405	2.457	2.473	-0.016	2.471	-0.014
	29856.944	4.918	4.919	-0.001	4.914	0.004
	29856.944	4.918	4.972	-0.054	4.964	-0.046
$5_{32} - 5_{23}$	21270.180		21270.173	0.007		
	21268.170	2.010	2.013	-0.003	2.016	-0.006
	21266.010	4.170	4.197	-0.027	4.180	-0.010
	21266.280	3.900	3.856	0.044	3.883	0.017
$5_{23} - 5_{14}$	19661.760		19661.774	-0.014		
	19660.350	1.410	1.416	-0.006	1.424	-0.014
	19658.920	2.840	2.838	0.002	2.863	-0.023
	19658.920	2.840	2.826	0.014	2.844	-0.004
$6_{33} - 6_{24}$	21080.450		21080.461	-0.011		
	21078.640	1.810	1.819	-0.009	1.828	-0.018
	21076.840	3.610	3.683	-0.073	3.703	-0.093
	21076.840	3.610	3.594	0.016	3.605	0.005
$6_{24} - 6_{15}$	26852.739		26852.726	0.013		
	26850.941	1.798	1.774	0.024	1.785	0.013
	26849.162	3.577	3.559	0.018	3.578	-0.001
	26849.162	3.577	3.537	0.040	3.568	0.009
$6_{42} - 6_{33}$	32994.562		32994.577	-0.015		
	32991.755	2.807	2.762	0.105	2.816	-0.009
	32987.851	6.711	6.695	0.016	6.633	0.078
	32989.887	4.675	4.122[c]	0.553	4.645	0.030
$6_{33} - 5_{42}$	38918.526		38918.501	0.025		
	B		-5.656		-5.015	
	B		-4.871		-4.757	
	B		-17.210		-14.945	
$7_{43} - 7_{34}$	29570.939		29570.941	-0.002		
	29568.126	2.813	2.776	0.037	2.809	0.004
	29565.054	5.885	5.912	-0.027	5.875	0.010
	29565.570	5.369	5.195	0.174	5.348	0.021
$7_{34} - 7_{25}$	23836.570		23836.568	0.002		
	23834.820	1.750	1.731	0.019	1.738	0.012
	23833.090	3.480	3.473	0.007	3.508	-0.028
	23833.090	3.480	3.451	0.029	3.473	0.007
$7_{43} - 6_{52}$	36445.481		36445.491	-0.010		
	B		-22.952		-18.968	
	B		-6.994		-6.875	
	B		-57.481		-48.535	
$8_{44} - 8_{35}$	27574.627		27574.619	0.008		
	27572.169	2.458	2.442	0.016	2.457	0.001
	27569.740	4.887	4.994	-0.107	5.000	-0.113
	27569.740	4.887	4.775	0.112	4.828	0.059
$8_{35} - 8_{26}$	29926.037		29926.054	-0.017		
	29924.163	1.874	1.870	0.004	1.887	-0.013
	29922.252	3.785	3.750	0.035	3.789	-0.004
	29922.252	3.785	3.728	0.057	3.773	0.012
$9_{45} - 9_{36}$	28463.000		28462.990	0.010		
	28460.864	2.136	2.122	0.014	2.148	-0.012
	28458.649	4.351	4.274	0.077	4.328	0.023
	28458.649	4.351	4.215	0.136	4.266	0.085

Table 1b.

Transition $J_{K-K+} - J'_{K-'K+'}$	ν_{exp}	$\Delta\nu_{exp}$	$\nu_{calc}^{(A_1A_1)}$ $\Delta\nu_{calc}^{PAM}$	$\delta\nu$	$\Delta\nu_{calc}^{IAM}$	$\delta\nu$
$(CH_3)_2{}^{77}Se$						
$2_{11} - 2_{02}$	9945.055		9945.047	0.008		
	9944.254	0.801	0.799	0.002	0.802	-0.001
	9943.464	1.591	1.602	-0.011	1.614	-0.023
	9943.464	1.591	1.593	-0.002	1.593	-0.002
$2_{21} - 2_{12}$	20580.083		20580.103	-0.020		
	20578.074	2.009	2.060	-0.051	2.046	-0.037
	20576.389	3.694	3.718	-0.024	3.709	-0.015
	20575.639	4.444	4.521	-0.077	4.477	-0.033
$2_{12} - 1_{01}$	25042.952		25042.906	0.046		
	25042.336	0.616	0.621	-0.005	0.625	-0.009
	25041.722	1.230	1.231	-0.001	1.238	-0.008
	25041.722	1.230	1.255	-0.025	1.259	-0.029
$2_{21} - 1_{10}$	38762.762		38762.735	0.027		
	38760.695	2.067	2.077	-0.010	2.065	0.002
	38759.035	3.727	3.714	0.013	3.705	0.022
	38758.283	4.479	4.593	-0.114	4.555	-0.076
$3_{21} - 3_{12}$	13708.925		13708.925	0.000		
	13707.667	1.258	1.256	0.002	1.254	0.004
	13706.344	2.581	2.584	-0.003	2.586	-0.005
	13706.467	2.458	2.441	0.017	2.438	0.020
$3_{12} - 3_{03}$	15476.204		15476.200	0.004		
	15475.059	1.145	1.135	0.010	1.143	0.002
	15473.927	2.277	2.276	0.001	2.285	-0.008
	15473.927	2.277	2.265	0.012	2.274	0.003
$3_{22} - 3_{13}$	24528.103		24528.151	-0.048		
	24526.029	2.074	2.142	-0.068	2.139	-0.065
	24523.875	4.228	4.205	0.023	4.199	0.029
	24523.875	4.228	4.364	-0.136	4.346	-0.118
$3_{13} - 2_{02}$	33271.191		33271.205	-0.014		
	33270.612	0.579	0.546	0.033	0.549	0.030
	33270.052	1.139	1.085	0.054	1.099	0.040
	33270.052	1.139	1.101	0.038	1.109	0.030
$3_{12} - 2_{21}$	23905.440		23905.480	-0.040		
	23906.350	-0.910	-0.907	-0.003	-0.880	-0.030
	23906.800	-1.360	-1.394	0.034	-1.365	0.005
	23907.640	-2.200	-2.232	+0.032	-2.164	-0.036
$4_{22} - 4_{13}$	15299.778		15299.785	-0.007		
	15298.513	1.265	1.260	0.005	1.262	0.003
	15297.250	2.528	2.534	-0.006	2.555	-0.027
	15297.250	2.528	2.505	0.023	2.506	0.022
$4_{13} - 4_{04}$	23311.480		23311.451	0.029		
	23309.820	1.660	1.656	0.004	1.662	-0.002
	23308.140	3.340	3.321	0.019	3.324	0.016
	23308.140	3.340	3.302	0.038	3.316	0.024
$4_{32} - 4_{23}$	30454.242		30454.229	0.013		
	30451.195	3.047	3.081	-0.034	3.031	0.016
	30448.749	5.493	5.483	0.010	5.465	0.028
	30447.563	6.679	6.840	-0.161	6.654	0.025
$4_{31} - 4_{22}$	23176.250		23176.257	-0.007		
	23174.170	2.080	2.010	0.070	2.035	0.045
	23171.590	4.660	4.699	-0.039	4.664	-0.004
	23172.760	3.490	3.345	0.145	3.475	0.015
$4_{23} - 4_{14}$	29796.132		29796.158	-0.026		
	29793.692	2.440	2.449	-0.009	2.449	-0.009
	29791.206	4.926	4.872	0.054	4.871	0.055
	29791.206	4.926	4.923	0.003	4.919	0.007
$5_{32} - 5_{23}$	21102.390		21102.408	-0.018		
	21100.400	1.990	1.982	0.008	1.984	0.006
	21098.290	4.100	4.128	-0.028	4.117	-0.017
	21098.570	3.820	3.800	0.020	3.832	-0.012
$5_{23} - 5_{14}$	19669.560		19669.555	0.005		
	19668.150	1.410	1.405	0.005	1.412	-0.002
	19666.740	2.820	2.816	0.004	2.836	-0.016
	19666.740	2.820	2.804	0.016	2.814	0.006
$6_{33} - 6_{24}$	30974.740		20974.727	0.013		
	20972.920	1.820	1.792	0.028	1.801	0.019
	20971.150	3.590	3.625	-0.035	3.648	-0.058
	20971.150	3.590	3.540	0.050	3.555	0.035
$6_{24} - 6_{15}$	26913.960		26913.927	0.033		
	26912.178	1.782	1.767	0.015	1.777	0.005
	26910.395	3.565	3.546	0.019	3.563	0.002
	26910.395	3.565	3.524	0.041	3.553	0.012
$6_{42} - 6_{33}$	32692.293		32692.277	0.016		
	32689.470	2.823	2.677	0.146	2.793	0.030
	32685.698	6.595	6.589	0.006	6.539	0.056
	32687.652	4.641	4.128 [c]	0.513	4.637	0.004
$7_{43} - 7_{34}$	29290.152		29290.161	-0.009		
	29287.389	2.763	2.731	0.032	2.766	-0.003
	29284.373	5.779	5.805	-0.026	5.781	-0.002
	29284.862	5.290	5.120	0.170	5.277	0.013
$7_{34} - 7_{25}$	23819.390		23819.381	0.009		
	23817.660	1.730	1.711	0.019	1.719	0.011
	23815.950	3.440	3.432	0.008	3.469	-0.029
	23815.950	3.440	3.411	0.029	3.434	0.006
$7_{43} - 6_{52}$	36814.844		36814.841	0.003		
	B		-22.294		-18.418	
	B		-6.867		-6.757	
	B		-56.286		-47.519	
$8_{44} - 8_{35}$	27370.871		27370.880	-0.009		
	27368.461	2.410	2.398	0.012	2.410	0.000
	27366.085	4.786	4.899	-0.113	4.906	-0.120
	27366.085	4.786	4.692	0.094	4.746	0.040
$8_{35} - 8_{26}$	30005.252		30005.281	-0.029		
	30003.356	1.896	1.859	0.037	1.875	0.021
	30001.475	3.777	3.729	0.048	3.766	0.011
	30001.475	3.777	3.706	0.071	3.746	0.031
$9_{45} - 9_{36}$	28382.103		28382.090	0.013		
	28379.976	2.127	2.088	0.039	2.117	0.010
	28377.872	4.231	4.203	0.028	4.266	-0.035
	28377.872	4.231	4.148	0.083	4.211	0.020

Table 1c.

$(CH_3)_2{}^{78}Se$

Transition $J_{K-K_+} - J'_{K'-K'_+}$	ν_{exp}	$\Delta\nu_{exp}$	$\nu_{calc}^{(A_1,A_1)}$ $\Delta\nu_{calc}^{PAM}$	$\delta\nu$	$\Delta\nu_{calc}^{IAM}$	$\delta\nu$
$1_{11} - 0_{00}$	15909.836		15909.879	-0.043		
	15909.224	0.612	0.632	-0.020	0.633	-0.021
	15908.604	1.232	1.234	-0.002	1.235	-0.003
	15908.604	1.232	1.296	-0.064	1.297	-0.065
$2_{11} - 2_{02}$	9927.907		9927.905	0.002		
	9927.119	0.788	0.796	-0.008	0.799	-0.011
	9926.332	1.575	1.595	-0.020	1.608	-0.033
	9926.332	1.575	1.587	-0.012	1.587	-0.012
$2_{21} - 2_{12}$	20489.318		20489.306	0.012		
	20487.285	2.033	2.044	-0.011	2.033	0.000
	20485.618	3.700	3.693	0.007	3.688	0.012
	20484.877	4.441	4.482	-0.041	4.442	-0.001
$2_{12} - 1_{01}$	24989.687		24989.730	-0.043		
	24989.073	0.614	0.617	-0.003	0.621	-0.007
	A		1.222		1.230	
	A		1.247		1.251	
$2_{21} - 1_{10}$	38649.012		38649.027	-0.015		
	38646.975	2.037	2.060	-0.023	2.051	-0.014
	38645.350	3.662	3.688	-0.026	3.684	-0.022
	38644.527	4.485	4.553	-0.068	4.521	-0.036
$3_{21} - 3_{12}$	13627.585		13627.588	-0.003		
	13626.341	1.244	1.244	0.000	1.244	0.000
	13625.042	2.543	2.559	-0.016	2.566	-0.023
	13625.161	2.424	2.419	0.005	2.421	0.003
$3_{12} - 3_{03}$	15482.654		15482.647	0.007		
	15481.525	1.129	1.135	-0.006	1.139	-0.010
	15480.385	2.269	2.275	-0.006	2.278	-0.009
	15480.385	2.269	2.264	0.005	2.268	0.001
$3_{22} - 3_{13}$	24449.824		24449.790	0.034		
	24447.659	2.165	2.130	0.035	2.128	0.037
	24445.540	4.284	4.182	0.102	4.180	0.104
	24445.540	4.284	4.339	-0.055	4.324	-0.040
$3_{12} - 2_{21}$	23998.430		23998.337	0.093		
	23999.310	-0.880	-0.887	+0.007	-0.866	-0.014
	23999.820	-1.390	-1.361	-0.029	-1.345	-0.045
	24000.580	-2.150	-2.185	0.035	-2.130	-0.020
$4_{22} - 4_{13}$	15255.680		15255.670	0.010		
	15254.426	1.254	1.251	0.003	1.255	-0.001
	15253.178	2.502	2.516	-0.014	2.537	-0.035
	15253.178	2.502	2.488	0.014	2.490	0.012
$4_{13} - 4_{04}$	23337.790		23337.792	-0.002		
	23336.110	1.680	1.658	0.022	1.660	0.020
	23334.450	3.340	3.325	0.015	3.320	0.020
	23334.450	3.340	3.307	0.033	3.313	0.027
$4_{32} - 4_{23}$	30307.699		30307.684	0.035		
	30304.681	3.018	3.052	-0.034	3.008	0.010
	30302.263	5.436	5.442	-0.006	5.434	0.002
	30301.104	6.595	6.765	-0.170	6.594	0.001
$4_{31} - 4_{22}$	22986.640		22986.629	0.011		
	22984.600	2.040	1.993	0.047	2.023	0.017
	22982.000	4.640	4.648	-0.008	4.629	0.011
	22983.160	3.480	3.328	0.152	3.469	0.011
$4_{23} - 4_{14}$	29732.490		29732.573	-0.083		
	29730.032	2.458	2.438	0.020	2.438	0.020
	29727.606	4.884	4.851	0.033	4.852	0.032
	29727.606	4.884	4.902	-0.018	4.899	-0.015
$5_{32} - 5_{23}$	20940.320		20940.315	0.005		
	20938.350	1.970	1.959	0.011	1.967	0.003
	20936.250	4.070	4.078	-0.008	4.078	-0.008
	20936.490	3.830	3.759	0.071	3.799	0.031
$5_{23} - 5_{14}$	19678.250		19678.234	0.016		
	19676.830	1.420	1.402	0.018	1.406	0.014
	19675.430	2.820	2.810	0.010	2.824	-0.004
	19675.430	2.820	2.798	0.022	2.805	0.015
$6_{33} - 6_{24}$	20873.840		20873.839	0.001		
	20872.060	1.780	1.772	0.008	1.781	-0.001
	20870.300	2.540	3.586	-0.046	3.609	-0.069
	20870.300	3.540	3.504	0.036	3.520	0.020
$6_{24} - 6_{15}$	26974.438		26974.350	0.088		
	26972.669	1.769	1.772	-0.003	1.773	-0.004
	26970.854	3.584	3.555	0.029	3.555	0.029
	26970.854	3.584	3.533	0.051	3.541	0.043
$6_{42} - 6_{33}$	32398.466		32398.460	0.006		
	32395.688	2.778	2.660	0.118	2.785	-0.007
	32391.974	6.492	6.514	-0.022	6.492	0.000
	32393.822	4.644	4.134[c]	0.510	4.652	-0.008
$7_{43} - 7_{34}$	29018.801		29018.776	0.025		
	29016.038	2.763	2.698	0.065	2.738	0.025
	29013.084	5.717	5.726	-0.009	5.719	-0.002
	A		5.065		5.226	
$7_{34} - 7_{25}$	23805.350		23805.346	0.004		
	23803.640	1.710	1.701	0.009	1.711	-0.001
	23801.930	3.420	3.411	0.009	3.445	-0.025
	23801.930	3.420	3.391	0.029	3.410	0.010
$7_{43} - 6_{52}$	37173.062		37173.115	-0.053		
	B		-21.810		-18.035	
	B		-6.768		-6.695	
	B		-55.466		-46.851	
$8_{44} - 8_{35}$	27176.242		27176.277	-0.035		
	27173.859	2.383	2.364	0.019	2.391	-0.008
	27171.516	4.726	4.829	-0.103	4.859	-0.133
	27171.516	4.726	4.630	0.096	4.699	0.027
$8_{35} - 8_{26}$	30084.873		30084.960	-0.087		
	30083.017	1.856	1.862	-0.006	1.867	-0.011
	30081.146	3.727	3.734	-0.007	3.750	-0.023
	30081.146	3.727	3.711	0.016	3.734	-0.007
$8_{53} - 7_{62}$	36168.739		36168.707	0.032		
	B		-42.154		-34.492	
	B		-8.505		-8.437	
	B		-89.625		-73.492	
$9_{45} - 9_{36}$	28308.445		28308.445	0.000		
	28306.342	2.103	2.065	0.038	2.086	0.017
	28304.246	4.199	4.156	0.043	4.203	-0.004
	28304.246	4.199	4.103	0.096	4.141	0.058
$13_{58} - 13_{49}$	43467.452		43467.439	0.013		
	43465.234	2.218	2.183[c]	0.035	2.218[c]	0.000
	43462.984	4.468	4.387[c]	0.081	4.468[c]	0.000
	43462.984	4.468	4.343[c]	0.125	4.468[c]	0.000

Table. 1d. (Headline as on p. 1226).

$(CH_3)_2{}^{80}Se$

$1_{11} - 0_{00}$	15829.140		15829.137	0.003		
	15828.524	0.616	0.625	-0.009	0.624	-0.008
	15827.900	1.240	1.220	0.020	1.217	0.023
	15827.900	1.240	1.282	-0.042	1.278	-0.038
$2_{11} - 2_{02}$	9895.202		9895.203	-0.001		
	9894.426	0.776	0.789	-0.013	0.790	-0.014
	9893.643	1.559	1.582	-0.023	1.590	-0.031
	9893.643	1.559	1.573	-0.014	1.570	-0.011
$2_{21} - 2_{12}$	20314.170		20314.119	0.051		
	20312.152	2.018	2.016	0.002	2.000	0.018
	20310.472	3.698	3.651	0.047	3.636	0.062
	20309.818	4.352	4.415	-0.063	4.363	-0.011
$2_{20} - 2_{11}$	13901.585		13901.577	0.008		
	13900.396	1.189	1.190	-0.001	1.188	0.001
	13898.844	2.741	2.761	-0.020	2.740	0.001
	13899.563	2.022	2.000	0.022	2.013	0.009
$2_{12} - 1_{01}$	24886.683		24886.689	-0.006		
	24886.109	0.574	0.610	-0.036	0.611	-0.037
	24885.574	1.109	1.208	-0.099	1.213	-0.104
	24885.574	1.109	1.233	-0.124	1.233	-0.124
$2_{21} - 1_{10}$	38429.208		38429.200	0.008		
	38427.199	2.009	2.034	-0.025	2.018	-0.009
	38425.597	3.611	3.648	-0.037	3.631	-0.020
	38424.784	4.424	4.487	-0.063	4.439	-0.015
$3_{21} - 3_{12}$	13471.513		13471.502	0.011		
	13470.285	1.228	1.227	0.001	1.224	0.004
	13469.000	2.513	2.522	-0.009	2.521	-0.008
	13469.115	2.398	2.387	0.011	2.382	0.016
$3_{12} - 3_{03}$	15495.838		15495.832	0.006		
	15494.713	1.125	1.128	-0.003	1.131	-0.006
	15493.580	2.258	2.261	-0.003	2.262	-0.004
	15493.580	2.258	2.251	0.007	2.251	0.007
$3_{22} - 3_{13}$	24298.808		24298.800	0.008		
	24296.705	2.103	2.108	-0.005	2.101	0.002
	24294.555	4.253	4.140	0.113	4.127	0.126
	24294.555	4.253	4.292	-0.039	4.267	-0.014
$3_{13} - 2_{02}$	33083.282		33083.298	-0.016		
	33082.796	0.486	0.535	-0.049	0.537	-0.051
	33082.297	0.985	1.063	-0.078	1.073	-0.088
	33082.297	0.985	1.079	-0.094	1.083	-0.098
$3_{12} - 2_{21}$	24177.670		24177.667	0.003		
	24178.510	-0.840	-0.861	0.021	-0.836	-0.004
	24178.980	-1.310	-1.323	0.013	-1.298	-0.062
	24179.740	-2.070	-2.122	0.052	-2.056	-0.014
$4_{22} - 4_{13}$	15172.574		15172.567	0.007		
	15171.342	1.232	1.235	-0.003	1.234	-0.002
	15170.111	2.463	2.483	-0.020	2.496	-0.033
	15170.111	2.463	2.456	0.007	2.451	0.012
$4_{13} - 4_{04}$	23388.760		23388.764	-0.004		
	23387.110	1.650	1.652	-0.002	1.653	-0.003
	23385.470	3.290	3.313	-0.023	3.307	-0.017
	23385.470	3.290	3.295	-0.005	3.299	-0.009
$4_{32} - 4_{23}$	30025.309		30025.383	-0.074		
	30022.369	2.940	3.003	-0.063	2.953	-0.013
	30019.972	5.337	5.377	-0.040	5.352	-0.015
	30018.884	6.425	6.636[c]	-0.211	6.449	-0.024
$4_{31} - 4_{22}$	22620.950		22620.946	0.004		
	22618.960	1.990	1.974	0.016	1.994	-0.004
	22616.410	4.540	4.578	-0.038	4.539	0.001
	22617.500	3.450	3.321	0.129	3.439	0.011
$4_{23} - 4_{14}$	29610.131		29610.144	-0.013		
	29607.710	2.421	2.417	0.004	2.409	0.012
	29605.325	4.806	4.810	-0.004	4.795	0.011
	29605.325	4.806	4.859	-0.053	4.841	-0.035
$5_{32} - 5_{23}$	20630.010		20630.001	0.009		
	20628.080	1.930	1.928	0.002	1.930	0.000
	20626.040	3.970	4.007	-0.037	3.992	-0.022
	20626.260	3.750	3.705	0.045	3.727	0.023
$5_{23} - 5_{14}$	19698.060		19698.054	0.006		
	19696.660	1.400	1.390	0.010	1.391	0.009
	19695.270	2.790	2.785	0.005	2.797	-0.007
	19695.270	2.790	2.773	0.017	2.777	0.013
$6_{33} - 6_{24}$	20684.320		20684.313	0.007		
	20682.580	1.740	1.741	-0.001	1.746	-0.006
	20680.850	3.470	3.521	-0.051	3.539	-0.069
	20680.850	3.470	3.446	0.024	3.453	0.017
$6_{24} - 6_{15}$	27093.345		27093.245	0.100		
	27091.573	1.772	1.766	0.006	1.766	0.006
	27089.763	3.582	3.543	0.039	3.539	0.043
	27089.763	3.582	3.520	0.062	3.525	0.057
$6_{42} - 6_{33}$	31831.062		31831.069	-0.007		
	31823.315	2.747	2.649	0.098	2.746	0.001
	31824.664	6.398	6.414	-0.016	6.352	0.046
	31826.424	4.638	4.185[c]	0.453	4.637	0.001
$7_{43} - 7_{34}$	28498.981		28498.962	0.019		
	28496.297	2.684	2.654	0.030	2.676	0.008
	28493.392	5.589	5.618	-0.029	5.586	0.003
	28493.835	5.146	5.000	0.146	5.133	0.013
$7_{34} - 7_{25}$	23785.700		23785.701	-0.001		
	23784.010	1.690	1.676	0.014	1.680	0.010
	23782.330	3.370	3.362	0.008	3.383	-0.013
	23782.330	3.370	3.343	0.027	3.348	0.022
$7_{43} - 6_{52}$	37879.134		37879.125	0.009		
	B		-20.911		-17.191	
	B		-6.658		-6.539	
	B		-53.929		-45.328	
$8_{44} - 8_{35}$	26810.126		26810.127	-0.001		
	26807.798	2.328	2.315	0.013	2.328	0.000
	26805.481	4.645	4.723	-0.078	4.734	-0.089
	26805.481	4.645	4.539	0.106	4.590	0.055
$8_{35} - 8_{26}$	30245.790		30245.901	-0.111		
	30243.923	1.867	1.848	0.019	1.852	0.015
	30242.070	3.720	3.708	0.012	3.719	0.001
	30242.070	3.720	3.684	0.036	3.703	0.017
$8_{53} - 7_{62}$	36951.217		36951.215	0.002		
	B		-41.465		-33.835	
	B		-8.376		-8.253	
	B		-88.325		-72.304	
$9_{45} - 9_{36}$	28180.278		28180.268	0.010		
	28178.228	2.050	2.022	0.028	2.047	0.003
	28176.184	4.094	4.068	0.026	4.109	-0.015
	28176.184	4.094	4.021	0.073	4.055	0.039
$9_{63} - 8_{72}$	37065.492		37065.498	-0.006		
	B		-58.978		-44.984	
	B		-9.989		-9.859	
	B		-130.234		-97.835	
$13_{58} - 13_{49}$	43871.521		43871.508	0.013		
	43869.306	2.215	2.165[c]	0.050	2.203[c]	0.012
	43867.088	4.433	4.353[c]	0.080	4.437[c]	-0.004
	43867.088	4.433	4.307[c]	0.126	4.437[c]	-0.004

Table 1e.

Transition $J_{K-K+} - J'_{K-K+}$	ν_{exp}	$\Delta\nu_{exp}$	$\nu_{calc}^{(A_1A_1)}$ $\Delta\nu_{calc}^{PAM}$	$\delta\nu$	$\Delta\nu_{calc}^{IAM}$	$\delta\nu$
$(CH_3)_2{}^{82}Se$						
$2_{11} - 2_{02}$	9864.538		9864.542	-0.004		
	9863.774	0.764	0.779	-0.015	0.781	-0.017
	9863.030	1.508	1.562	-0.054	1.572	-0.064
	9863.030	1.508	1.554	-0.046	1.553	-0.045
$2_{21} - 2_{12}$	20147.367		20147.356	0.011		
	20145.398	1.969	1.986	-0.017	1.972	-0.003
	20143.776	3.591	3.604	-0.013	3.593	-0.002
	20143.067	4.300	4.339	-0.039	4.295	0.005
$2_{12} - 1_{01}$	24788.250		24788.257	-0.007		
	24787.733	0.517	0.602	-0.085	0.604	-0.087
	24786.965	1.285	1.193	0.092	1.199	0.086
	24786.965	1.285	1.216	0.069	1.219	0.066
$2_{21} - 1_{10}$	38219.617		38219.594	0.023		
	38217.622	1.995	2.002	-0.007	1.990	0.005
	38216.025	3.592	3.599	-0.007	3.589	0.003
	38215.260	4.357	4.408	-0.051	4.370	-0.013
$3_{21} - 3_{12}$	13324.051		13324.027	0.024		
	13322.849	1.202	1.210	-0.008	1.205	-0.003
	13321.601	2.450	2.483	-0.033	2.484	-0.034
	13321.690	2.361	2.354	0.007	2.350	0.011
$3_{12} - 3_{03}$	15509.292		15509.313	-0.021		
	15508.182	1.110	1.116	-0.006	1.121	-0.011
	15507.059	2.233	2.237	-0.004	2.242	-0.009
	15507.059	2.233	2.226	0.007	2.231	0.002
$3_{22} - 3_{13}$	24155.413		24155.402	0.011		
	24153.325	2.088	2.088	0.008	2.075	0.013
	24151.218	4.195	4.088	0.107	4.078	0.117
	24151.218	4.195	4.233	-0.038	4.213	-0.018
$3_{13} - 2_{02}$	32965.037		32965.050	-0.013		
	32964.515	0.522	0.528	-0.006	0.530	-0.008
	32964.004	1.033	1.049	-0.016	1.061	-0.028
	32964.004	1.033	1.064	-0.031	1.071	-0.038
$4_{22} - 4_{13}$	15095.993		15096.000	-0.007		
	15094.782	1.211	1.216	-0.005	1.218	-0.007
	15093.571	2.422	2.445	-0.023	2.463	-0.041
	15093.571	2.422	2.420	0.002	2.419	0.003
$4_{13} - 4_{04}$	23437.560		23437.560	0.000		
	23435.930	1.630	1.637	-0.007	1.642	-0.012
	23434.270	3.290	3.283	0.007	3.283	0.007
	23434.270	3.290	3.265	0.025	3.276	0.014
$4_{32} - 4_{23}$	29757.233		29757.269	-0.063		
	29754.293	2.940	2.950	-0.010	2.904	0.036
	29751.948	5.285	5.304	-0.019	5.285	0.000
	29750.898	6.335	6.497	-0.162	6.332	0.003
$4_{31} - 4_{22}$	22273.190		22273.174	0.016		
	22271.230	1.960	1.955	0.005	1.975	-0.015
	22268.740	4.450	4.507	-0.057	4.473	-0.023
	22269.750	3.440	3.317	0.123	3.426	0.014
$4_{23} - 4_{14}$	29494.137		29494.170	-0.033		
	29491.634	2.503	2.388	0.115	2.387	0.116
	29489.394	4.743	4.752	-0.009	4.746	-0.003
	29489.394	4.743	4.799	-0.056	4.790	-0.047
$5_{32} - 5_{23}$	20337.816		20337.812	0.004		
	20335.924	1.892	1.897	-0.005	1.898	-0.006
	20333.915	3.901	3.937	-0.036	3.926	-0.025
	20334.153	3.663	3.652	0.011	3.674	-0.011
$5_{23} - 5_{14}$	19720.730		19720.735	-0.005		
	19719.350	1.380	1.371	0.009	1.377	0.003
	19717.970	2.760	2.747	0.013	2.766	-0.006
	19717.970	2.760	2.735	0.025	2.748	0.012
$6_{33} - 6_{24}$	20510.406		20510.423	-0.017		
	20508.669	1.737	1.709	0.028	1.711	0.026
	20506.998	3.408	3.453	-0.045	3.469	-0.061
	20506.998	3.408	3.383	0.025	3.387	0.021
$6_{24} - 6_{15}$	27209.334		27209.271	0.063		
	27207.608	1.726	1.748	-0.022	1.758	-0.032
	27205.851	3.483	3.507	-0.024	3.516	-0.033
	27205.851	3.483	3.483	0.000	3.506	-0.023
$6_{42} - 6_{33}$	31290.555		31290.543	0.012		
	31287.829	2.726	2.638	0.088	2.734	-0.008
	31284.262	6.293	6.317	-0.024	6.273	0.020
	31285.904	4.651	4.238 [C]	0.413	4.660	-0.009
$7_{43} - 7_{34}$	28009.339		28009.351	-0.012		
	28006.703	2.636	2.613	0.023	2.637	-0.001
	28003.864	5.475	5.513	-0.038	5.484	-0.009
	28004.277	5.062	4.939	0.123	5.063	-0.001
$7_{34} - 7_{25}$	23776.280		23776.267	0.013		
	23774.620	1.660	1.646	0.014	1.656	0.004
	23772.950	3.330	3.300	0.030	3.336	-0.006
	23772.950	3.330	3.281	0.049	3.301	0.029
$7_{43} - 6_{52}$	38556.865		38556.864	0.001		
	B		-19.969		-16.437	
	B		-6.567		-6.460	
	B		-52.235		-43.937	
$8_{44} - 8_{35}$	26473.624		26473.625	-0.001		
	26471.341	2.283	2.266	0.017	2.281	0.002
	26469.054	4.570	4.617	-0.047	4.633	-0.063
	26469.054	4.570	4.449	0.121	4.496	0.074
$8_{35} - 8_{26}$	30407.815		30407.851	-0.036		
	30405.947	1.868	1.822	0.046	1.832	0.036
	30404.138	3.677	3.656	0.021	3.680	-0.003
	30404.138	3.677	3.631	0.046	3.664	0.013
$9_{45} - 9_{36}$	28075.759		28075.744			
	28073.742	2.017	1.975	0.042	2.000	0.017
	28071.744	4.015	3.971	0.044	4.031	-0.016
	28071.744	4.015	3.928	0.087	3.984	0.031

A not resolved, B not measured, C not used for fitting.

Table 2. Rotational constants [GHz] and centrifugal distortion constants [GHz] for dimethyl selenide in the order of Table 1, calculated with equal sets of transitions of Table 1. The τ-centrifugal distortion constants [GHz] were derived from those of (1). Moments of inertia Ig [AMUÅ^2] calculated with conversion factor $5.05376 \cdot 10^5$ AMUÅ^2 MHz [14]. $\varkappa$ asymmetry parameter, in brackets doubled standard error, standard deviation [KHz] nineth line.

	^{76}Se	^{77}Se	^{78}Se	^{80}Se	^{82}Se
A	11.442978(7)	11.405953(8)	11.369972(16)	11.300409(19)	11.234103(12)
B	6.912763(7)	6.912807(8)	6.912844(17)	6.912862(19)	6.912885(13)
C	4.551511(6)	4.545652(7)	4.539929(14)	4.528768(17)	4.518053(11)
$\Delta_J \cdot 10^5$	0.492 (20)	0.611 (23)	0.932 (45)	0.808 (52)	0.722 (34)
$\Delta_{JK} \cdot 10^4$	-0.333 (6)	-0.323 (7)	-0.325 (13)	-0.330 (15)	-0.327 (10)
$\Delta_K \cdot 10^4$	0.869 (10)	0.847 (12)	0.847 (23)	0.852 (27)	0.840 (17)
$\delta_J \cdot 10^5$	0.339 (6)	0.348 (6)	0.345 (13)	0.341 (14)	0.345 (9)
$\delta_K \cdot 10^6$	0.27 (48)	-0.63 (55)	-0.35 (107)	-0.01 (121)	-0.43 (78)
	15	18	35	41	27
$\tau'_{aaaa} \cdot 10^3$	-0.234	-0.234	-0.246	-0.241	-0.234
$\tau'_{bbbb} \cdot 10^4$	-0.468	-0.523	-0.649	-0.596	-0.565
$\tau'_{cccc} \cdot 10^5$	0.744	0.337	0.966	0.506	0.124
$\tau_1 \cdot 10^4$	0.743	0.557	0.181	0.353	0.440
$\tau_2 \cdot 10^3$	0.348	0.207	-0.0771	0.0540	0.121
I_a	44.1647	44.3081	44.4483	44.7219	44.9859
I_b	73.1077	73.1072	73.1068	73.1066	73.1064
I_c	111.0348	111.1779	111.3180	111.5924	111.8570
$\varkappa$	-0.31473	-0.30990	-0.30515	-0.29586	-0.28683

Table 3. Correlation matrix of the fitted constants of Table 2 for $(CH_3)_2{}^{76}Se$. Most unfavorable case.

1.00							
0.49	1.00						
0.68	0.80	1.00					
0.48	0.02	0.45	1.00				
-0.13	0.25	-0.18	-0.89	1.00			
0.32	-0.34	0.10	0.92	-0.91	1.00		
-0.10	0.37	-0.15	-0.79	0.93	-0.83	1.00	
0.08	-0.27	0.16	0.81	-0.97	0.83	-0.96	1.00

The IAM-analysis was performed according to the treatment of Woods [11, 12]. By a version of his program modified by Meier [13] and Lutz we got the results given in Table 5. $W(1)$ and θ was fitted.

The moment of inertia $I_\alpha = 3.244$ AMU Å^2 of the methyl group was taken from [1] for both methods as I_α is strongly correlated to V_3. The correlation coefficient of the two fitted parameters is about 0.7 in both cases.

	^{76}Se	^{77}Se	^{78}Se	^{80}Se	^{82}Se
s	42.11	42.14	42.13	42.13	42.16
F	166.146	166.115	155.083	166.038	166.002
V_3	1500.9 (19)	1501.7 (15)	1501.1 (13)	1500.7 (13)	1501.5 (14)
Θ	39.63 (16)	39.67 (13)	39.73 (11)	36.69 (11)	39.58 (12)
N	24	24	24	26	23
δ	70	56	48	49	52
$\overline{\Delta\nu}_{exp}$	2.923	2.936	2.937	2.710	2.894

Table 4. Internal rotation parameters of the PAM analysis for dimethyl selenide in the order of Table 1. $I_\alpha = 3.244$ AMUÅ^2 assumed. N Number of transitions, δ standard deviation of the fit [nHz], $\overline{\Delta\nu}_{exp}$ mean of splittings [MHz], s reduced barrier, F rotational constant of methyl-group [GHz], V_3 hindering potential [cal/mole], θ angle between internal rotation and a-xis [degree].

	^{76}Se	^{77}Se	^{78}Se	^{80}Se	^{82}Se
W (1)	-1.6112(77)	-1.6048(48)	-1.6060(47)	-1.6032(58)	-1.5988(51)
s	42.06 (3)	42.09 (1)	42.09 (2)	42.10 (2)	42.12 (2)
F	165.997	165.970	165.946	165.898	165.863
V_3	1498.0 (13)	1498.8 (8)	1498.4 (9)	1498.4 (10)	1498.8 (9)
Θ	39.87 (11)	39.90 (7)	39.90 (7)	39.91 (9)	39.80 (8)
N	24	24	24	26	23
δ	51	33	31	37	36
$\overline{\Delta\nu}_{exp}$	2.948	2.960	2.962	2.783	2.920
ϱ	0.06314	0.06297	0.06281	0.06250	0.06226
Δ_0	-90.289	-89.892	-89.945	-89.766	-89.478
β	0.4674	0.4690	0.4704	0.4730	0.4737

Table 5. Internal rotation parameters of the IAM analysis for dimethyl selenide in the order of Table 1. $W(1)$ Fourier coefficient see [5, 6, 11] ϱ, Δ_0[MHz], β [rad] IAM-Parameters [11] see also Table 4.

As can be seen from Tables 4 and 5 the values for the hindering potential V_3 and the angle θ between internal rotation and a-axis agree within the error limits for each method. As assumed no isotopic effect of the selenium substitution can be observed.

There is a slight difference between the results of both methods. The fit of the IAM seems to be superior to that of PAM indicated by the standard deviation. For single components we observed a good fit for IAM but not for PAM.

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