A Contribution to the Analysis of the Rotational Spectra of Dimethyl Selenide in Torsional Excited States

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Z. Naturforsch. **38 a,** 1346–1358 (1983); received August 22, 1983

Rotational spectra of dimethyl selenide in torsional and vibrational excited states were measured by Stark- and MWMW double resonance spectroscopy. The spectra could be assigned partially and evaluated for internal rotation parameters. The limitation of the rigid top-rigid frame Hamiltonian became obvious.

Introduction

With this paper we continue a series of investigations of molecules of the type $(CH_3)_2X$, $X = O$, S, CH_2 and SiH_2 [1, 2, 3], $(CD_3)_2$ X, X = O, S, Se [1, 3, 4] aiming at the barrier to internal rotation of the methyl groups. The barrier of these two top molecules of C_{2v}-configuration symmetry with two equivalent tops is given by a two dimensional Fouriers series:

$$V(\alpha_1, \alpha_2) = \frac{V_3}{2}(1 - \cos 3\alpha_1) + \frac{V_3}{2}(1 - \cos 3\alpha_2) + V'_{12} \sin 3\alpha_1 \sin 3\alpha_2 + V_{12} \cos 3\alpha_1 \cos 3\alpha_2 + \dots \quad (1)$$

V_3 is the hindering potential, V'_{12} and V_{12} are top-top coupling potential coefficients, α_i the torsion angles.

The analysis of the rotational spectra of $(CH_3)_2{}^{78}Se$ and $(CH_3)_2{}^{80}Se$ is based on a rigid frame rigid top Hamiltonian. In the course of our study we noticed its limitations. As it was discussed earlier [5–11] we will give it in equation (2) in short.

The Hamiltonian includes only two degrees of freedom for internal rotation (torsion) and three for overall rotation. Vibrations are neglected. The measurements of a rotational spectrum in an excited vibrational state showed a different effective potential V_3 indicating a torsion-vibration interaction.

The rotational spectra of $(CH_3)_2{}^nSe$ in the groundstate were investigated by [12, 13] for the five isotopes $n = 75$, 76, 78, 80, and 82 and the potential barrier V_3 has been determined from the multiplet splittings. It is known from the other molecules of this type that for the determination of V'_{12} and V_{12} the analysis of torsion excited states is necessary.

Experimental

The spectra of $(CH_3)_2Se$ were recorded by means of a conventional Stark spectrometer [14, 15] equipped with an 8 m absorption cell using 33 kHz Stark modulation. Dimethyl selenide [16] was prepared according to Bird and Challenger [17] by M. Andolfatto. Isotopic enriched Se (99.2%) was obtained from Rohstoff-Einfuhr GmbH, Düsseldorf. The sample pressure was around 5 mTorr, the temperatures were between −30 and +20 °C.

For the assignment microwave-microwave double resonance experiments (MWMWDR) were necessary. For this investigation we extended the range of our MWMWDR spectrometer [18, 19] to pump frequencies from 18 to 26.5 GHz [20].

Assignment of the Spectra

The first problem of this work was the assignment of the spectra with respect to the rotational transitions and the vibrational and torsional states. The problem is still further complicated, as five isotopic species are observable. Taking the lowest vibrational and the six lowest torsional states $\tilde{v}_n = 0_1$, 1_1, 1_2, 2_1, 2_2, 2_3 [1], each divided in four sublevels, 120 rotational spectra are overlayed for the five isotopic species.

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[1] For designation see [2].

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As the ground state $\tilde{v}_n = 0_1$ rotational spectra were thoroughly investigated [13] 20 spectra were precisely known.

The assignment to the isotopic species was made by transferring the isotopic shift from the ground to the excited states, by intensity arguments and comparison of the spectra of natural isotopic composition with those of ^{80}Se enriched to 99%[1].

So the ^{80}Se species (49.8% natural abundance) could clearly be assigned. The ^{78}Se species (23.5%) was identified by intensity and typical shifts. As the other species are less abundant, we concentrated on the problem of assignment for these two species.

As was pointed out in [1] different features of the spectrum aid in assignment. We repeat them for discussion:

a) Stark effect;
b) relative spin weights [9, 10];
c) Boltzmann factor of different states;
d) Fit of A_iA_j-rotational lines[2] to a quasi rigid rotor spectrum;
e) Theoretical predictions of the torsional splittings according Hamiltonian (2);
f) Similarities of frequency shifts with respect to ground state of Q-branch series of $(CH_3)_2Se$ and $(CD_3)_2Se$;
g) Double resonances.

As the spectrum is quite dense the Stark effect pattern is frequently disturbed by other lines. But the different types of Stark effect, a linear contribution for A_iE, EE-species ($i = 1, 2$) lines helped.

The relative spin weights and Boltzmann factor is useful only for comparison of lines not too different in frequency, as intensity measurements with a conventional Stark spectrometer are difficult. The widest splitting of an identified multiplet was 267 MHz.

We noticed that only four spectra could be fitted to quasi rigid rotor spectra with a mean square deviation less than 2.5 MHz. For one isotopic species and the states $\tilde{v} = 1, 2$ five should be present. Further we failed in many cases for fitting the internal rotation splittings consistently. Also similarities between $(CH_3)_2Se$ and $(CD_3)_2Se$ were of minor use.

[1] Enriched selenium for the other isotopes are available but expensive.
[2] For group theoretical labelling see [9, 10].

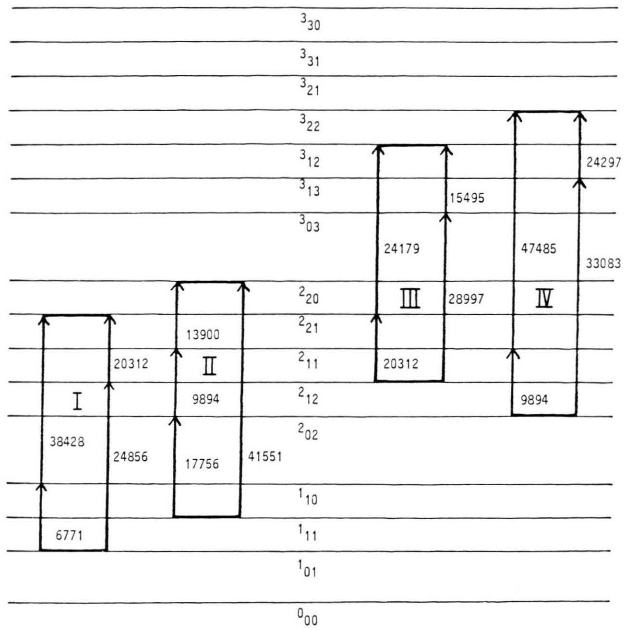

Fig. 1. Energy level scheme of dimethyl selenide. The energy level difference between the levels are not in scale. The Ritz cycles I to IV are indicated by strong arrows. Frequencies near the transition arrows are the ground state values of the isotop ^{80}Se [MHz].

We exploited very much the double resonance technique. As the spectrum is very dense and the double resonance is not always decisive because of off resonance pumping and a poor signal to noise ratio we used as a check the Ritz combination principle of terms as illustrated in Figure 1.

This procedure was limited to low J lines to minimize centrifugal distortion effects (compare point d) above) and reduce computing time (compare point e) above).

In Fig. 1 we have indicated Ritz "cycles" I to IV. Cycle I and III and II and IV are connected by one transition respectively. The lines of cycle I determine only the rotational constants A and C, but the cycles I + III and/or II + IV should be sufficient to determine the rotational constants A, B and C if the spectrum follows a quasi rigid rotor pattern.

In Table 1 to 4 we give the lines for cycles I to IV measured by DR- and/or Stark spectroscopy. They are not yet identified for their torsional state $\tilde{v}_n > 0_1$ and isotopic species except ^{80}Se. Frequencies indicated with "$\Rightarrow$" were calculated by the combination principle[1].

[1] For a more detailed tabulation see [21].

Table 1. Measured frequencies of $(CH_3)_2Se$ [MHz]. Transitions $(J_{K_- K_+} - J'_{K'_- K'_+})$ of Ritz cycle I (see Figure 1). ⟷ or DR: measured by double resonance experiments. L: linear Stark effect contribution. RR: rigid rotor fit possible. ⇒: calculated by the combination principle. Measured by Stark spectroscopy: S 1: with reduced precision (uncertainty < 150 kHz). S 2: with full precision (uncertainty < 50 kHz).

Cycle I
Isotop Se 80:

1 10 − 1 01	2 12 − 1 01	2 21 − 1 10	2 21 − 2 12	
←	→			
←		→	Com. principle	Stark spectroscopy
6 731.65	24 910.799	38 497.028	⇒ 20 317.88	S 2 20 318.057
S 2 .685	S 2 .877	S 2 .177	.985	
6 749.15	24 922.148	38 487.317	⇒ 20 314.32	S 2 20 314.252
S 2 .077	S 2 .200	S 2 .317	.194	
L 6 765.81	24 958.080	38 584.641	⇒ 20 392.37	S 1 20 392.27
S 2 .768	S 1 .08	S 1 4.68	.37	
6 780.33	24 927.816	38 320.522	⇒ 20 173.03	S 1 20 172.82
S 2 .29	S 2 8.037	S 1 .65	2.90	
6 803.68	24 700.615	38 632.572	⇒ 20 735.63	S 1 20 735.620
S 2 .684	S 2 .636	S 2 .396	.444	
RR 6 806.90	24 879.508	38 492.952	⇒ 20 420.34	S 2 20 420.338
S 2 .725	S 2 .508	S 2 .970	.187	
RR 6 811.17	24 836.972	38 458.008	⇒ 20 432.21	S 2 20 432.340
S 2 .300	S 2 .972	S 2 .222	.550	
L 6 826.24	24 728.734	38 683.603	⇒ 20 781.11	S 2 20 781.208
S 2 .280	S 2 .695	S 2 .615	.200	
L 6 830.73	24 726.394	38 625.493	⇒ 20 729.83	S 2 20 729.871
S 1 .735	S 2 .369	S 2 .454	.82	
RR 6 849.96	24 923.097	38 621.340	⇒ 20 548.20	S 1 20 548.36
S 2 50.041	S 2 .110	S 1 .340	.27	
6 853.30	24 722.208	38 468.148	⇒ 20 599.24	S 1 20 599.18
S 1 .31	S 2 .247	S 2 .109	.07	
L 6 856.94	24 897.344	38 319.948	⇒ 20 279.55	S 1 20 279.74
S 2 5.045	S 2 .344	S 1 20.07	.77	
6 870.50	24 932.938	38 629.237	⇒ 20 566.80	S 1 20 567.17
S 1 .50	S 2 .938	S 1 .22	.78	
Isotopes except Se 80				
6 777.71	24 610.811	238 313.532	⇒ 20 480.43	S 1 20 480.16
S 2 .686	S 2 .890			
6 798.71	25 010.015	38 715.603	⇒ 20 504.30	S 2 20 504.20
S 2 .637	S 2 .170	S 2 .788	.28	
6 815.09	25 020.428	38 703.142	⇒ 20 497.80	S 2 20 497.88
S 2 .072	S 2 .423	S 2 .123	.77	
6 847.71	25 026.967	38 534.194	⇒ 20 354.94	S 1 20 354.98
S 2 .714	S 2 .954			
RR 6 865.45	24 982.000	38 712.346	⇒ 20 595.80	S 1 20 595.66
	S 2 .000			
6 916.10	25 000.083	38 535.375	⇒ 20 451.39	S 1 20 451.23

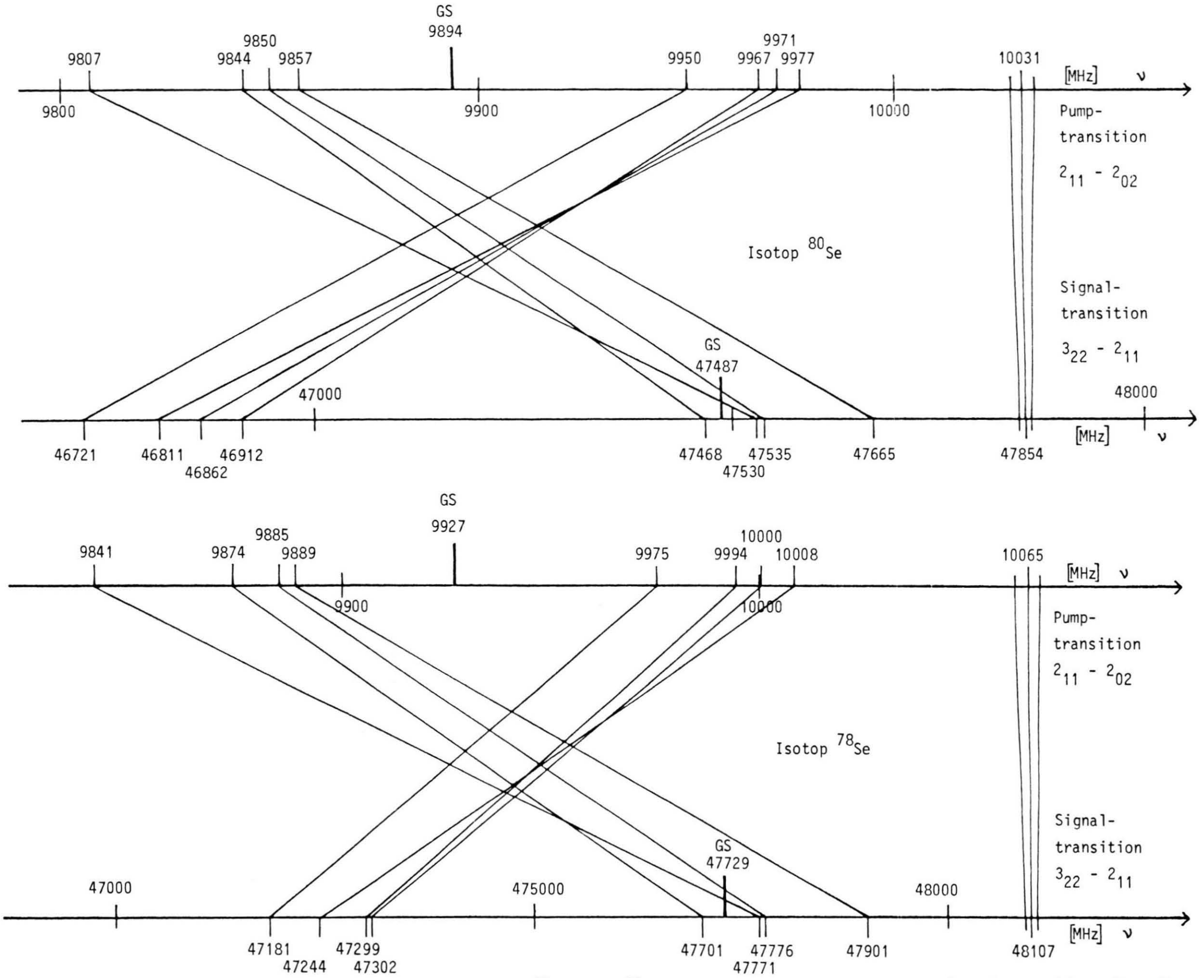

Fig. 2. Double resonance diagram of the two isotopes ^{78}Se and ^{80}Se. Pump transition: $2_{11}-2_{02}$; signal transition: $3_{22}-2_{11}$. GS: ground state value.

For the search of double resonances diagrams as given in Fig. 2 were useful. Both isotopic forms have similar spectra.

Analysis of the Spectra

For the analysis a symmetrized Hamiltonian based on the rigid frame-rigid top model is used. The symbols are given in [9].

$$
\begin{aligned}
H = {} & C' P_x^2 + B' P_y^2 + A' P_z^2 \\
& + \tfrac{1}{2} F_+ p_+^2 + \tfrac{1}{2} F_- p_-^2 + V_3(1 - \cos 3\alpha_+ \cos 3\alpha_-) \\
& + \tfrac{1}{2} (V_{12} - V'_{12}) \cos 6\alpha_+ \\
& + \tfrac{1}{2} (V_{12} + V'_{12}) \cos 6\alpha_- \\
& - 2F_+ \frac{I_\alpha}{I_y} \lambda_y P_y p_+ - 2F_- \frac{I_\alpha}{I_z} \lambda_z P_z p_- . \qquad (2)
\end{aligned}
$$

Discussions of the model and the Hamiltonian (also in equivalent forms) may be found in [2, 5–11, 22]. Usually the Hamiltonian matrix is diagonalised in two steps. First a van Vleck transformation is applied to a torsional $\tilde{v}_n$-level or two near degenerate torsional $\tilde{v}_n$-levels. Second the effective rotational matrix is diagonalised. This procedure may be separated for the $A_i A_j$, $A_i E$, EA_j and EE, $i, j = 1, 2$, torsional sublevels. For second order van Vleck transformation an approximate quasi rigid rotor spectrum results for the $A_i A_j$-levels [1].

[1] We estimated that matrix elements arising from the operators with p_+ and p_- by van Vleck transformation and connecting the near degenerate states $\tilde{v}_n = 1_1$ and 1_2 are still negligible.

Table 2. Measured frequencies of $(CH_3)_2Se$ [MHz]. Transitions of Ritz cycle II.

Cycle II

Isotop Se 80

2 11 − 2 02	2 20 − 2 11	2 02 − 1 11	2 20 − 1 11
9 843.985 ↔	14 135.467		
9 843.82 ↔	—	17 511.760	⇒ 41 491.21
9 850.66 ↔	14 440.192		
9 850.66 ↔	—	17 524.698	⇒ 41 815.55
9 857.625 ↔	14 281.216 ↔	—	41 627.490
9 857.630 ↔	—	17 488.842 ↔	41 627.480
9 949.785 ↔	14 013.000 ↔	—	41 579.762
9 950.030 ↔	—	17 617.002 ↔	41 579.724
9 967.378 ↔	14 171.001 ↔	—	41 756.915
9 967.680 ↔	—	17 618.514 ↔	41 756.927

Isotopes except Se 80

2 11 − 2 02	2 20 − 2 11	2 02 − 1 11	2 20 − 1 11
9 942.60 ↔	13 984.039	⇒ 17 649.42	
	13 983.975 ↔	—	41 576.062
9 975.05 ↔	14 209.545		
9 974.94 ↔	—	17 583.920 ↔	41 768.430
9 994.377 ↔	14 383.158 ↔	—	41 963.343
9 994.50 ↔	—	17 586.114 ↔	41 963.671
9 994.52 ↔	13 939.92	⇒ 17 585.90	
	13 940.26 ↔	—	41 520.341
10 008.27 ↔	—	17 596.968 ↔	42 112.537
	⇒ 14 507.30		

Table 3. Measured frequencies of $(CH_3)_2Se$ [MHz]. Transitions of Ritz cycle III and double resonance connection to Ritz cycle I (Table 1).

Isotop Se 80

Cycle III				connected to cycle I
3 03 − 2 12	3 12 − 3 03	3 12 − 2 21	2 21 − 2 12	2 21 − 1 10
29 097.39 ↔	15 580.42 ↔	24 363.530		
		24 363.587 ↔	20 314.25 ↔	38 487.317
29 097.40 ↔	—	—	20 314.28	
29 119.82 ↔	15 706.560			
29 119.83 ↔	—	—	20 318.057 ↔	38 497.177
		⇒ 24 508.32		
28 796.55 ↔	15 637.520 ↔	23 704.240		
		23 704.272 ↔	20 729.871 ↔	38 625.454
28 796.46 ↔	—	—	20 729.829	
		23 664.387 ↔	20 735.62 ↔	38 632.396
28 796.019 ↔	—	—	20 735.682	
	⇒ 15 603.99			

In Tables 5 and 6 we give cycles of type I + III and II + IV, connected by measured transitions $2_{21}-2_{12}$ and $2_{11}-2_{02}$ respectively. They are selected from Tables 1 to 4. For these a rigid rotor spectrum fit was tried. Only three cycles of type II + IV showed a standard deviation less or equal 3.3 MHz. With a prediction of rigid rotor spectra these cycles could be connected to three cycles of type I (see Table 1).

In a similar way one cycle of type IV $2_{11}-2_{02}$: 9841 MHz (^{78}Se) could be connected to one cycle of type I $1_{10}-1_{01}$: 6865 MHz, see Table 1. The results are summarized in Table 7 together with results for the ground state [13].

For the two most abundant isotopes up to state $\tilde{v}_n = 2_3$ ten quasi rigid rotor spectra should have been found. We interpret this failure by a break down of the approximation used in handling (2) or (2) itself[1].

Taking the lines of the four spectra as A_iA_j-components of the torsional multiplet we tried to assign the EE-components, as those are the most intense in a multiplet of a rotational transition.

For this purpose the splittings $(\nu_{EE}-\nu_{A_iA_j})$ were calculated with a program[2] based on Hamiltonian (2). The van Vleck transformation was applied to the levels $(\tilde{v}_n = 1_1, 1_2)$, $(\tilde{v}_n = 2_1, 2_2)$ and $\tilde{v}_n = 2_3$. Denominator correction is included.

Out of a very large number of trials only one consistent choice of measured dubletts resulted. The frequencies of the lines are given in Table 8.

The rotational transitions $1_{11}-0_{00}$, $2_{02}-1_{11}$, $3_{03}-2_{12}$ and $3_{21}-3_{12}$ of Table 8 and marked with *a* were assigned with additional rigid rotor calculations for the A_iA_j species and calculations of the torsional splittings $\nu_{EE}-\nu_{A_iA_j}$.

For the fitting $s = 4V_3/9F = 42.13$ and $I_\alpha = 3.244$ amuÅ^2 was taken from the ground state analysis [12]. $\beta = \arccos \lambda_{bi}$, V'_{12} and V_{12}, were varied. We noticed, that for the states $\tilde{v}_n = 1_2$ and $\tilde{v}_n = 2_3$

[1] It cannot be absolutely excluded that some spectra have been overlooked.

[2] The computerprogram MELITA original written by A. Trinkhaus [2] and modified by V. Typke, Ulm [3] was adapted to the Digital PDP 10 of the Rechenzentrum, University Kiel.

Table 4. Measured frequencies of $(CH_3)_2Se$ [MHz]. Transitions of Ritz cycle IV.

Cycle IV
Isotop Se 80

2 11 − 2 02	3 13 − 2 02	3 22 − 2 11	3 22 − 3 13 Comb. princ.	Stark spect.	
9 445.840	33 161.310	47 777.119	⇒ 24 061.649	S 1	24 061.63
9 465.530	33 169.130	47 794.906	⇒ 24 091.306	S 1	24 090.50
9 500.233	33 158.358	47 869.876	⇒ 24 211.751	DR	24 212.00
9 807.135	33 066.650	47 529.865	⇒ 24 270.350	S 1	24 270.50
9 843.980	32 996.104	47 468.297	⇒ 24 316.173	S 1	24 316.25
9 850.530	33 086.731	47 535.373	⇒ 24 299.172	DR	24 299.00
9 857.407	33 108.185	47 865.375	⇒ 24 414.597	S 1	24 414.75
9 898.490	33 095.231	47 427.676	⇒ 24 230.935	S 1	24 231.13
9 949.785	32 794.259	46 720.865	⇒ 23 876.391	S 1	23 876.38
9 967.387	32 825.390	46 912.357	⇒ 24 054.354	S 1	24 054.38
9 971.475	32 822.789	46 862.328	⇒ 24 011.014	S 1	24 010.63
9 977.085	32 819.576	46 811.290	⇒ 23 968.799	S 1	23 968.75
10 010.305	33 132.563	47 348.016	⇒ 24 225.758	DR	24 226.00
10 160.510	33 223.720	48 186.441	⇒ 25 123.231	S 1	25 123.70
10 170.630	33 213.908	47 739.242	⇒ 24 695.964	S 1	24 696.00
10 178.00	33 233.169	48 339.464	⇒ 25 284.477	S 1	25 284.25
10 192.19	33 243.508	48 273.710	⇒ 25 222.392	S 1	25 222.24
10 198.762	33 266.227	48 310.288	⇒ 25 242.823	S 1	25 243.04
10 201.10	33 316.707	48 401.551	⇒ 25 285.944	S 1	25.285.68
Isotopes except Se 80					
9 818.602	32 968.513	47 305.911	⇒ 24 156.00	GS	Se 82
9 828.42	32 992.109	47 440.621	⇒ 24 276.932	S 1	24 277.00
9 840.630	33 190.176	47 771.303	⇒ 24 421.757	S 1	24 421.88
9 884.685	33 210.521	47 775.855	⇒ 24 450.019	GS	Se 78
9 888.920	33 229.650	47 900.673	⇒ 24 559.943	S 1	24 560.15
9 975.050	32 942.785	47 180.887	⇒ 24 213.152	S 1	24 313.13
9 994.377	32 969.798	47 298.551	⇒ 24 323.130	S 1	24 323.18
10 000.570	32 970.828	47 301.711	⇒ 24 331.453	S 1	24 331.25
10 008.050	32 967.360	47 244.278	⇒ 24 284.968	S 1	24 284.75
10 008.60	33 043.051	47 475.157	⇒ 24 440.706	S 1	24 440.88
10 023.96	33 117.556	47 434.291	⇒ 24 340.695	S 1	24 240.5
10 049.19	33 254.395	47 555.125	⇒ 24 349.920	S 1	24 350.0
10 208.14	33 339.276	47 975.594	⇒ 24 844.458	S 1	24 844.72

GS Se 82, GS Se 78: The lines are disturbed by the ground state transitions of the two isotopes.

Table 5. Transitions of Ritz cycles I/III [MHz].

Isotop Se 80

1 10 − 1 01	2 12 − 1 01	2 20 − 1 10	2 21 − 2 12	3 12 − 2 21	3 12 − 3 03	3 03 − 2 12	*a*	*b*
6 731.685	24 910.877	38 497.177	20 318.057	⇒ 24 508.32	15 706.56	29 119.83	6	32
L 6 750.077	24 922.200	38 487.317	20 314.252	24 363.56	15 580.42	29 097.40	7	14
6 803.684	24 700.636	38 632.396	20 735.620	23 664.39	⇒ 15 603.99	28 796.02	6	110
L 6 830.735	24 726.369	38 625.454	20 729.871	23 704.26	15 637.52	28 796.50	7	80

L: Linear Stark effect contribution. Rigid rotor Fit. *a*: Number of fitted lines. *b*: Standard deviation of the fit (in MHz!).

Table 6. Transitions of Ritz cycles II/IV [MHz].

Isotop Se 80

2 20 – 1 10	2 20 – 2 11	2 02 – 1 11	2 11 – 2 02	3 13 – 2 02	3 22 – 2 11	3 22 – 3 13	*a*	*b*	*c*
	14 173.350		9 807.135	33 066.650	47 529.865	⇒ 24 270.35	4	0.22	6807
⇒ 41 491.21	14 135.467	17 511.760	9 843.980	32 996.104	47 468.297	⇒ 24 316.17	5	1.01	6811
⇒ 41 815.45	14 440.192	17 524.698	9 850.563	33 086.731	47 535.373	24 299.00	6	107	–
41 627.49	14 281.216	17 488.842	9 857.567	33 108.185	47 665.375	⇒ 24 414.76	6	3.3	6850
41 579.74	14 013.000	17 717.002	9 949.785	32 794.259	46 720.865	⇒ 23 876.39	6	279	–
41 756.92	14 171.001	17 618.514	9 967.378	32 825.390	46 912.357	⇒ 24 054.35	6	276	–
		17 629.404	9 977.085	32 819.576	46 811.290	⇒ 23 968.80	4	211	–

Isotopes except Se 80

2 20 – 1 11	2 20 – 2 11	2 02 – 1 11	2 11 – 2 02	3 13 – 2 02	3 22 – 2 11	3 22 – 3 13	*a*	*b*	*c*
	14 249.542		9 818.602	32 968.513	47 305.911	⇒ 24 156.00	4	102	–
		17 490.678	9 884.66	33 210.521	47 775.855	⇒ 24 450.02	4	31	–
41 768.430	14 209.545	17 583.920	9 975.050	32 942.785	47 180.887	⇒ 24 213.15	6	191	–
41 963.343	14 383.158	17 586.114	9 994.40	32 969.798	47 298.551	⇒ 24 323.13	6	227	–
		17 551.86	10 024.00	33 117.556	47 434.291	⇒ 24 340.695	4	177	–
		17 579.40	10 049.14	33 254.395	47 555.125	⇒ 24 349.920	4	218	–

Rigid rotor fit. *a*: Number of fitted lines; *b*: Standard deviation of the fit (in MHz!); *c*: Connected to further transitions (Cycle I, see Table 1).

Table 7. Rotational constants of $(CH_3)_2Se$ for four sets of transitions [GHz]. Frequencies and standard deviation [MHz]. Ritz cycle I: see Table 1. Ritz cycles II/IV: see Table 6, for ^{78}Se cycle IV only, see Table 4.

Cycle I	Cycles II/IV	Rigid rotor fit		Rotational constants		
		Number of transitions	Standard deviation	*A*	*B*	*C*
^{80}Se Ground state		Dreizler et al. [13], Table 2		11.300409	6.912862	4.528768
6807	9807	8	0.21	11.324998 −0.024589	6.830035 0.082827	4.518184 0.010584[a]
6811	9844	9	1.1	11.317001	6.838930	4.506392
6850	9858	10	2.5	11.368313	6.836530	4.518578
^{78}Se Ground state		Dreizler et al. [13], Table 2		11.369972	6.912844	4.539929
6865	9841	8	0.25	11.394471 −0.024499	6.829975 0.082869	4.529195 0.010734[a]

[a] Difference to the ground state value.

the fit was nearly of the same quality as given in Table 9. This ambiguity could be removed, as only the data resulting from the choice $\tilde{v}_n = 2_3$ give an infrared torsion transition of 147.2 cm^{-1} whereas other results in 135.6 cm^{-1}. For this transition Durig and Winther [23, 24] reported 147.5 cm^{-1}.

The final result is given in Table 10 and compared with the results for $(CH_3)_2O$ and $(CH_3)_2S$. The parameter V_{12} is undetermined for $(CH_3)_2Se$.

Analysis of a vibration excited state

The problem of the analysis of torsional excited states is reflected by the analysis of a vibrational excited state, which was assigned in the course of the measurements with the help of double resonance experiments. As this state is torsion ground state it should show torsional splittings of the rotational lines equal to the ground state if no interaction is present. The experimental result is different. The

Table 8. Rotational lines of $(CH_3)_2Se$ for the $\bar{v}_n = 2_3$ state [MHz]. The measured frequencies ν_{exp} are given in order of the symmetry species A_1A_1, EE. $\Delta\nu$ gives the torsional splitting referred to the A_1A_1 component $\delta\nu$ is the deviation between calculated and measured splittings: $\delta\nu = |\Delta\nu_{exp} - \Delta\nu_{calc}|$. Characterization: see Table 1. [a] see text.

Transition	Isotop	Char	ν_{exp}	$\Delta\nu_{exp}$	$\Delta\nu_{calc}$	$\delta\nu$
1 10 – 1 01	Se 80	DR, S 1	6 806.725			
		DR	6 857.045	50.320	49.43	0.89
	Se 78	DR	6 865.45			
		DR	6 916.10	50.65	50.25	0.40
1 11 – 0 00[a]	Se 80	S 1	15 842.73			
		S 1	15 844.77	2.04	1.64	0.40
	Se 78	S 1	15 923.48			
		S 1	15 925.35	1.87	1.71	0.16
2 11 – 2 02	Se 80	DR	9 807.135			
		DR, S 2	9 850.563	43.428	43.22	0.21
	Se 78	DR	9 840.630			
		DR	9 884.685	44.055	44.02	0.04
2 21 – 2 12	Se 80	DR, S 2	20 420.338			
		DR	20 279.74	−140.60	−140.55	0.05
	Se 78	Ko, S 1	20 595.66			
		Ko, S 1	20 451.23	−144.43	−144.37	0.06
2 20 – 2 11	Se 80	DR	14 173.35			
		DR	14 440.192	266.842	266.64	0.21
2 02 – 1 11[a]	Se 80	S 1	17 513.43			
		DR	17 524.698	11.27	11.98	0.71
2 12 – 1 01	Se 80	DR, S 2	24 879.508			
		DR, S 2	24 897.344	17.836	17.50	0.33
	Se 78	DR, S 2	24 982.000			
		DR	25 000.083	18.083	17.82	0.26
2 21 – 1 10	Se 80	DR, S 2	38 492.970			
		DR	38 319.948	−173.022	−172.48	0.54
	Se 78	DR	38 712.346			
		DR	38 535.375	−176.971	−176.80	0.17
3 22 – 3 13	Se 80	Ko	24 270.350			
		DR	24 299.000	28.650	28.75	0.10
	Se 78	Ko	24 421.757			
		Ko	24 450.019	28.262	28.35	0.09
3 21 – 3 12[a]	Se 80	S 1	13 651.875			
		S 1	13 760.175	108.30	109.25	0.95
	Se 78	S 1	13 810.425			
		S 1	13 922.025	111.60	112.11	0.51
3 03 – 2 12[a]	Se 80	S 1	28 743.45			
		S 1	28 749.00	5.55	5.30	0.25
	Se 78	S 1	28 749.60			
		S 1	28 754.85	5.25	5.35	0.10
3 13 – 2 02	Se 80	DR	33 066.650			
		DR	33 086.731	20.081	19.40	0.68
	Se 78	DR	33 190.176			
		DR	33 210.521	20.345	19.77	0.58
3 22 – 2 11	Se 80	DR	47 529.865			
		DR	47 535.373	5.508	4.93	0.58
	Se 78	DR	47 771.303			
		DR	47 775.855	4.552	4.10	0.46

Table 9. Results of the analysis of the torsional fine structure. The uncertainties shown in parentheses are in units of the last digit and are standard errors. Parameters fixed at the ground state values: $V_3 = 1501 \frac{\text{cal}}{\text{mol}}$ ($s = 42.13$), $I_\alpha = 3.244$ amuÅ^2, conversion factor: 505.376 amuÅ^2 GHz. Correlation between V_{12} and V'_{12} (typical values): 0.996 for $\tilde{v} = 1_1$, 0.614 for $\tilde{v} = 2_3$. Standard deviation should be compared with mean splitting $\overline{\Delta\nu_{exp}} = \sum_i^n \Delta\nu_{exp,i}/n$ of approx. 65 MHz.

Isotop	Number of splittings	Torsional state	Fitted parameters β [°]	V_{12} [GHz]	V'_{12} [GHz]	Standard deviation [MHz]
^{80}Se	13	1_2	50.20 (26)	1120 (48)	530 (88)	0.62
		2_3	49.95 (31)	3 (58)	341.1 (51)	0.61
	11	1_2	49.83 (39)	1154 (47)	481 (68)	0.60
		2_3	49.65 (41)	35 (60)	339.2 (60)	0.62
^{78}Se	11	1_2	49.99 (24)	1181 (26)	443 (28)	0.37
		2_3	49.78 (25)	75 (36)	352.6 (34)	0.37

Table 10. Final results of the torsional fine structure analysis and comparison of the torsional parameters. Assumptions in square brackets.

Molecule	$(CH_3)_2Se$			$(CD_3)_2Se$
Torsional state, isotop	GS, ^{80}Se	$\tilde{v}_n = 2_3$, ^{80}Se	$\tilde{v}_n = 2_3$, ^{78}Se	$\tilde{v}_n = 1_n$, ^{80}Se
s	42.13 (2)	[42.13]	[42.13]	79.2 (5)
V_3 $\left[\frac{\text{cal}}{\text{mol}}\right]$	1500.7 (7)	[1500.7]	[1501.1]	1493 (5)
V_{12} $\left[\frac{\text{cal}}{\text{mol}}\right]$	–	0.2 (53)	7.2 (34)	–
V'_{12} $\left[\frac{\text{cal}}{\text{mol}}\right]$	–	32.5 (5)	33.6 (4)	28.4 (3)
β [°]	50.31 (6)	49.95 (31)	49.78 (25)	50.02 (11)
F [GHz]	166.04	165.98	166.01	87.85
F' [GHz]	–	−4.32	−4.31	−3.61

[$I_\alpha = 3.244$ amuÅ^2]

Eigenvalues of the torsional excited states in GHz (by program MELITA): $\tilde{v}_n = 0_1$: 4652.490, $\tilde{v}_n = 1_1$: 9067.245, $\tilde{v}_n = 1_2$: 9113.050, $\tilde{v}_n = 2_1$: 13 000.88, $\tilde{v}_n = 2_2$: 13 000.93, $\tilde{v}_n = 2_3$: 13 530.17, $\tilde{v}_n = 3_1$: 16 685.25

	V_3 $\left[\frac{\text{cal}}{\text{mol}}\right]$	V'_{12} $\left[\frac{\text{cal}}{\text{mol}}\right]$	I_α [amuÅ^2]	Reference
$(CH_3)_2O$	2618 (4)	18 (8)	3.2084	Lutz [1]
$(CD_3)_2O$	2572 (6)	29 (12)	6.4294	Lutz [1]
$(CH_3)_2S$	2136 (2)	34 (4)	3.204	Demaison [3]
$(CD_3)_2S$	2097.3 (4)	32.2 (5)	6.403	Demaison [3]
$(CH_3)_2Se$	1501 (1)	32.5 (5)	3.244	this work [21]
$(CD_3)_2Se$	1493 (5)	28.4 (3)	6.35	Pandey [18]

Table 11. Rotational lines of $(CH_3)_2Se$ [MHz] for a vibrational excited state. The frequencies are given in the order of the symmetry species A_1A_1, EE, A_1E and EA_1. ν_{exp} gives the measured frequencies, $\Delta\nu_{exp}$ the measured splittings. ν_{calc} was calculated by centrifugal distortion analysis, $\Delta\nu_{calc}$ are the calculated splittings (IAM method, see Table 12). $\delta\nu$ is the deviation between calculated and measured splittings: $\delta\nu = |\Delta\nu_{exp} - \Delta\nu_{calc}|$.

Transition	Isotop	ν_{exp}	$\Delta\nu_{exp}$	$\nu_{calc}, \Delta\nu_{calc}$	$\delta\nu$
1 10 − 1 01	Se 80	6 917.22		6 917.208	
		6 915.47	1.75	1.816	0.07
		6 913.40	3.82	4.059	0.24
				3.205	
2 11 − 2 02	Se 80	10 033.958		10 033.965	
		10 030.886	3.072	3.172	0.100
				6.485	
		10 027.810	6.148	6.203	0.055
	Se 78	10 068.092		10 067.981	
		10 064.970	3.122	3.226	0.104
				6.599	
		10 061.840	6.252	6.305	0.053
2 21 − 2 12	Se 80	20 750.870		20 750.853	
		20 742.180	8.690	8.677	0.013
		20 738.770	12.100	12.134	0.034
				22.461	
	Se 78	20 928.85		20 928.925	
		20 919.72	9.13	8.979	0.15
		20 916.42	12.43	12.438	0.01
				23.350	
2 20 − 2 11	Se 80	14 305.125		14 305.131	
		14 304.030	1.095	1.123	0.028
				7.464	
		14 308.005	−2.880	−2.864	0.016
	Se 78	14 502.255		14 502.366	
		14 501.175	1.080	1.097	0.017
				7.712	
		14 505.540	−3.285	−3.201	0.084
2 12 − 1 01	Se 80	24 990.502		24 990.505	
		24 988.489	2.013	2.091	0.078
		24 986.617	3.885	4.040	0.155
				4.323	
	Se 78	25 094.138		25 094.149	
		25 092.071	2.067	2.144	0.077
		25 089.770	4.368	4.141	0.227
				4.435	
2 21 − 1 10	Se 80	38 824.184		38 824.150	
		38 815.205	8.979	8.951	0.028
		38 812.003	12.181	12.115	0.066
				23.578	
	Se 78	39 046.440		39 046.560	
		39 037.120	9.320	9.264	0.056
		39 033.992	12.448	12.418	0.030
				24.513	
3 12 − 3 03	Se 80	15 622.505		15 622.517	
		15 617.207	5.298	5.385	0.087
		15 711.280	11.225	10.845	0.380
				10.699	
3 22 − 3 13	Se 80	24 738.750		24 738.779	
		24 730.710	8.040	8.035	0.005
		24 723.690	15.060	15.070	0.010
				17.071	

Table 11 (continued)

Transition	Isotop	ν_{exp}	$\Delta\nu_{exp}$	$\nu_{calc}, \Delta\nu_{calc}$	$\delta\nu$
3 21 − 3 12	Se 80	13 817.525		13 817.523	
		13 814.346	3.179	3.241	0.062
		13 810.346	7.179	7.482	0.303
		13 812.018	5.507	5.481	0.026
	Se 78	13 977.521		13 977.319	
		13 974.277	3.244	3.315	0.071
		13 970.13	7.39	7.690	0.30
		13 972.02	5.50	5.572	0.07
3 13 − 2 02	Se 80	33 156.125		33 156.127	
		33 154.459	1.666	1.753	0.087
				3.435	
		33 152.690	3.435	3.581	0.146
	Se 78	33 280.592		33 280.531	
		33 278.845	1.747	1.801	0.054
				3.525	
		33 276.994	3.598	3.678	0.080
3 03 − 2 12	Se 80	28 868.850		28 868.819	
		28 867.966	0.884	0.893	0.009
		28 866.900	1.960	1.925	0.025
				1.643	
	Se 78	28 875.942		28 876.028	
		28 875.033	0.909	0.886	0.023
		28 873.950	1.992	1.919	0.073
				1.626	
3 12 − 2 21	Se 80	23 740.45		23 740.484	
		23 743.00	−2.55	−2.399	0.15
		23 739.95	0.50	0.637	0.14
				−10.119	
	Se 78	23 558.172		23 558.078	
		23 560.999	−2.827	−2.639	0.188
		23 557.848	0.324	0.464	0.140
				−10.895	
3 22 − 2 11	Se 80	47 860.909		47 860.940	
		47 854.319	6.590	6.617	0.027
		47 848.884	12.025	12.020	0.005
		47 846.586	14.323	14.449	0.126
	Se 78	48 105.407		48 105.327	
		48 098.554	6.853	6.801	0.052
		48 092.988	12.419	12.321	0.098
		48 090.518	14.889	14.885	0.004
4 13 − 4 04	Se 80	23 535.944		23 535.919	
		23 527.812	8.132	8.325	0.193
				16.701	
		23 519.232	16.712	16.601	0.111
	Se 78	23 485.632		23 485.653	
		23 477.268	8.364	8.425	0.061
				16.902	
		23 468.676	16.956	16.798	0.158
4 22 − 4 13	Se 80	15 432.082		15 432.047	
		15 427.755	4.327	4.511	0.184
				9.346	
		15 423.470	8.612	8.698	0.086
	Se 78	15 519.609		15 519.825	
		15 515.156	4.453	4.584	0.031
				9.510	
		15 510.829	8.780	8.825	0.045

Table 11. (continued)

Transition	Isotop	ν_{exp}	$\Delta\nu_{exp}$	$\nu_{calc}, \Delta\nu_{calc}$	$\delta\nu$
4 32 − 4 23	Se 80	30 703.555		30 703.589	
		30 690.860	12.695	12.686	0.009
		30 686.381	17.174	17.313	0.139
		30 670.168	33.387	33.229	0.158
	Se 78	30 991.376		30 991.226	
		30 978.160	13.22	13.209	0.01
		30 973.680	17.70	17.554	0.15
				34.832	
4 04 − 3 13	Se 80	39 217.770		39 217.768	
		39 216.580	1.190	1.217	0.027
				2.506	
		39 215.530	2.240	2.359	0.119
	Se 78	39 273.740		39 273.732	
		39 272.505	1.235	1.227	0.008
				2.529	
		39 271.450	2.290	2.377	0.087
4 13 − 3 22	Se 80	38 014.918		38 014.909	
		38 013.466	1.452	1.507	0.055
		38 010.752	4.166	4.137	0.029
				1.889	
	Se 78	37 866.553		37 866.608	
		37 865.139	1.414	1.426	0.012
		37 862.400	4.153	4.037	0.116
				1.663	
6 42 − 6 33	Se 80	32 926.605		32 926.596	
		32 925.615	0.990	0.922	0.068
				14.648	
		32 937.165	−10.560	−10.426	0.134
	Se 78	33 500.97		33 501.006	
		33 500.12	0.85	0.656	0.19
				15.273	
		33 513.04	−12.07	−12.008	0.06

Table 12. Results of the analysis of a vibrational excited state. a) Rotational [GHz] and centrifugal distortion [kHz] constants according to van Eijck. Highest correlation between D'_{JK} and D'_K: 0.94. b) Internal rotation parameters. Highest correlation between β and s: 0.46. The uncertainties shown in parentheses are in units of the last digit and are standard errors. $I_\alpha = 3.244$ amuÅ^2, conversion factor: 505.376 amuÅ^2 GHz.

	$(CH_3)_2{}^{80}Se$	$(CH_3)_2{}^{78}Se$
A	11.435585 (7)	11.505991 (37)
B	6.908975 (9)	6.908974 (49)
C	4.518313 (6)	4.529426 (31)
D'_J	7.55 (24)	7.79 (123)
D'_{JK}	−29.2 (8)	−15.8 (38)
D'_K	87.2 (15)	62.7 (74)
δ_J	3.40 (10)	3.15 (59)
R'_6	0.305 (44)	−0.985 (222)
Number of transitions	19	17
Standard deviation [kHz]	29	144

Table 12 (continued)

	$(CH_3)_2{}^{78}Se$	$(CH_3)_2{}^{80}Se$
β [°]	42.40 (5)	42.35 (5)
$V_3 \left[\frac{\text{cal}}{\text{mol}}\right]$	1133.2 (4)	1135.4 (4)
s	31.94 (2)	32.01 (2)
F [GHz]	165.366	165.325
Standard deviation [kHz]	104	109

splittings are wider, the measurements are given in Table 11.

In Table 12 we give the result for the rotational and centrifugal distortion constants. The Hamiltonian of van Eijck [25, 26] was applied to the $A_i A_j$-components.

The torsional analysis was in principle based on the Hamiltonian (2) with $V'_{12} = 0$, $V_{12} = 0$, $F' = 0$ treated with the internal axis method [5, 6, 27–29]. It should be pointed out that this Hamiltonian should be considered as an effective one as torsion-vibration interaction is neglected. As can be seen from Table 11 the fit is good, but the results of the torsion analysis illustrate especially by β that the Hamiltonian is only effective. An unreasonable angle of 84.7° between the internal rotation axis results.

From the intensity we estimated that the vibrational excited state is the first CSeC bending state at 209 cm^{-1} [20].

Discussion

We noticed, that the Hamiltonian (2) is only partially sufficient for explaining some features of the spectrum, others are unexplained. It would be possible to generalize this Hamiltonian as it was done for one methyl top molecules [30] and applied to some molecules [31]. We did not yet start this work as the computing time would be very high.

We thank the members of our group for help and discussions, the Deutsche Forschungsgemeinschaft and Fonds der Chemie for funds. The very extended calculations were made at the University computer center partially funded by the Deutsche Forschungsgemeinschaft.

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