Microwave Spectrum of hexa-Deutero Dimethyl Selenide in the Ground and Excited Torsional States

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The ground state rotational spectra of ^{80}Se and ^{78}Se species of the hexadeutero dimethyl selenide have been measured in the region from 5 to 40 GHz. In both the cases, rotational and centrifugal distortion constants have been determined by a least square fit to about thirty transition frequencies. For the $(CD_3)_2{}^{80}Se$ molecule, fourteen rotational transitions in the excited torsional states $\tilde{v}=1_1$ and $\tilde{v}=1_2$ were also recorded, out of which nine appeared as well resolved triplets. The potential barrier parameter V_3 and the angle α between one of the 'top axes' and the 'b axis' have been determined by a least square fit of the mean value of the observed splittings in the $\tilde{v}=1_1$ and 1_2 states. The methyl top moment of inertia I_α was kept fixed at 6.35 amu Å^2, which is half of the observed inertia defect in the molecule.

Introduction

The microwave spectroscopic investigation of molecules possessing two internally rotating tops has become a subject of current interest, particularly from the aspect of top-top coupling [1]. For this purpose, the assignment of the microwave spectrum of the molecule in the ground ($\tilde{v}=0_1$) and at least two excited torsional states ($\tilde{v}=1_1$ and 1_2) * is required. Relatively few detailed studies of this kind have been made. Dimethyl selenide was chosen as a part of the general program of studying the barrier and top-top coupling parameters in molecules with the general formula $(CH_3)_2-X$, where X is a group VI atom. The dimethyl sulphide molecule has already been studied [2–4]. Dimethyl ether is currently being studied [5, 6]. We hope that a systematic study of this kind yields information regarding how the barrier, the tilt of the axis of the methyl top with respect to the X – C bond, the top-top coupling and other molecular parameters change with the change of the X atom in this series of molecules. This in turn is expected to throw some light on the nature of the intramolecular forces and the origin of potential barrier hindering internal angular motion of the tops in the molecule.

We have made the start from the hexadeuterated species of the molecule for two reasons. Firstly our past experiences with other molecules of the series and a model calculation on this molecule told us that the excited torsional state rotational transitions for the hexadeuterated species should appear as closely spaced triplets with a characteristic intensity ratio, making thereby their assignment somewhat easier. The corresponding fine structure of the excited torsional state rotational transitions for the hydrogenated species of the molecule is expected to be very widely spaced (within at least 50 – 200 MHz) for even low J transitions. In this frequency range, the relative intensity of the fine structure component lines does not become readily apparent, because of the variations in the input microwave power. This makes the assignment somewhat difficult. Secondly, even the ground state spectrum of the hexadeuterated species was not assigned. The ground state work on the corresponding hydrogenated and some other species of the molecule has been done by Beecher [7].

Experimental

The hexadeuterated dimethyl selenide was prepared by refluxing deuterated methyl iodide over a slurry of selenium powder in an alkaline solution of sodium formaldehyde-sulfoxylate as described by Bird and Challenger [8]. The species of ^{80}Se and ^{78}Se species were observed in natural abundance.

The microwave spectrum was recorded with a conventional 33 KHz Stark modulation spectrograph, employing phase stabilized BWO's as radiation sources and an automatic system of recording the frequency markers [9]. The spectrograph is equip-

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* We use the notations of Ref. [1] for the torsional energy levels: $\tilde{v}=1_1$ and 1_2 correspond to mixtures of the states $v_1 v_2=01$ and $v_1 v_2=10$ with $E_{1_1} \leqq E_{1_2}$.

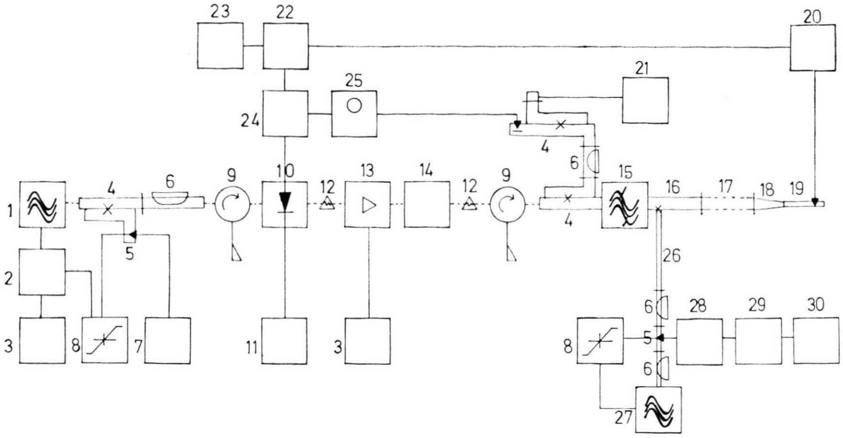

Fig. 1. Schematic block diagram of the microwave—microwave double resonance spectrograph.

1. BWO, CSF 4032 B for 8—16 GHz; Watkins Johnson 2056-6 for 12.4—18 GHz. — 2. Modulator for beam voltage correction. — 3. Power supply, FXR 817A or equivalent. — 4. Directional coupler 3 db or 10 db. — 5. Mixer. — 6. Variable attenuator. — 7. Frequency decade, Schomandl FD 3, 300—1000 MHz. — 8. Syncriminator, Schomandl FDS 30, 30 MHz. — 9. Circulator. — 10. Pin modulator, Alpha Industries MT 3486. — 11. Pin power supply. — 12. Attenuator 3 db. — 13. TWT, Varian VTX 6084 for 8—12.4 GHz; Hughes 848 HD for 12.4—18 GHz. — 14. Low pass filter, Sage L12MA049 for 12 GHz; Sage L18MA050 for 18 GHz. — 15. Band pass filter, AIL. — 16. Directional coupler [14], 10 db. — 17. X-band absorption cell (11 meter). — 18. Taper, X to Q or X to K band. — 19. Suitable waveguide cut off filter and detector. — 20. Preamplifier. — 21. Microwave power meter, Marconi Instruments Ltd. Type 6460. — 22. Phase sensitive detector, Ithaca Dynatrac 391A. — 23. Recorder. — 24. Pulse generator, hp 8005A. — 25. Dual beam oscilloscope, Tektronix 475. — 26. Suitable combination of tapers and waveguide filters. — 27. Microwave sweeper, hp 8690 B, 18—26.5 GHz or 26.5—40 GHz. — 28. Frequency standard, Rohde & Schwarz XUC, 470—1000 MHz. — 29. Frequency synthesizer, Rohde & Schwarz SMDH, 20—30 MHz. — 30. Digital sweeper. — - - - - Microwave coaxial cable; ═══ Waveguide.

ped with an eight meter absorption cell and is operating in the range from 5 to 40 GHz. The frequency measurements are believed to be accurate within ±0.03 MHz.

For the purpose of assigning the excited torsional state spectrum of the $(\mathrm{CD_3})_2{}^{80}\mathrm{Se}$ molecule, use was also made of a microwave-microwave double resonance spectrograph in which both the pump and the signal frequencies could be phase stabilized and varied. The block diagram of the experimental setup is shown in Figure 1. The radiation source for the pump was a TWT amplifier driven by a phase stabilized BWO. Output powers are 2 Watt (Varian VTX 6084) in X-band and 10 Watt (Hughes 848 HD) in KU-band. The pump source is on-off amplitude modulated by a pin diode switch (Alpha Industries, MT 3486). The rise and fall times of the microwave bursts as obtained from the pin modulator were less than 100 nsec and not noticeably modified by the TWT. A low pass filter after the TWT is essential for the suppression of harmonics of the TWT. The pump frequency could be varied from 8 to 18 GHz and the signal frequency from 16 to 40 GHz.

Ground State Spectrum

The ground state spectrum of both $(\mathrm{CD_3})_2{}^{80}\mathrm{Se}$ and $(\mathrm{CD_3})_2{}^{78}\mathrm{Se}$ molecules were assigned using conventional methods. Later, while assigning the excited torsional state transitions of the molecule with the help of microwave-microwave double resonance experiments, some of the ground state transitions of the $(\mathrm{CD_3})_2{}^{80}\mathrm{Se}$ molecule were also confirmed. The measured ground state rotational transitions of the $(\mathrm{CD_3})_2{}^{80}\mathrm{Se}$ and $(\mathrm{CD_3})_2{}^{78}\mathrm{Se}$ molecules are given in Tables I and II respectively. None of these transitions were found to split by the coupling between overall and internal rotation angular momenta. The rotational constants are determined by fitting the observed frequencies to an eight parameter centrifugal distorted rotor according to Watson [10]. The rotational constants, centrifugal distortion constants, and the moments of inertia are given in Table III.

First Excited Torsional State Spectrum and Barrier to Internal Rotation in the Molecule

The rotational transitions of the molecule in both of the first excited torsional states $\tilde{v} = 1_1$ and 1_2 were in general expected to consist of quartets, the components of which could suitably be characterized by the $A_1 A_2 : E E : A_1 E : E A_2$ and $A_2 A_1 : E E : A_2 E : E A_1$ species of the group $C_{3v}^- \otimes C_{3v}^+$. The

Table I. Measured ground state rotational transitions of the $(CD_3)_2{}^{80}Se$ molecule. All frequencies are in MHz.

Transition $J_{K_-K_+}-J'_{K'_-K'_+}$	Observed frequency	Calculated frequency *
$1_{11}-0_{00}$	12385.76	12385.712
$1_{10}-1_{01}$	5179.08	5179.064
$2_{20}-2_{11}$	10940.22 [a]	10940.213
$2_{11}-2_{02}$	7355.11	7355.101
$2_{21}-2_{12}$	15536.87 [a]	15536.851
$2_{12}-1_{01}$	19592.34	19592.350
$2_{21}-1_{10}$	29950.14 [a]	29950.137
$2_{20}-1_{11}$	32126.12 [a]	32126.152
$2_{02}-1_{11}$	13830.85 [a]	13830.838
$3_{30}-3_{21}$	19818.25	19818.244
$3_{21}-3_{12}$	10478.73	10478.710
$3_{12}-3_{03}$	11254.46	11254.440
$3_{22}-3_{13}$	18345.48	18345.468
$3_{22}-2_{11}$	37156.82 [a]	37156.799
$3_{03}-2_{12}$	22704.66 [a]	22704.662
$3_{12}-2_{21}$	18422.24	18422.251
$4_{31}-4_{22}$	18008.18	18008.195
$4_{22}-4_{13}$	11431.76	11431.778
$4_{13}-4_{04}$	16848.35	16848.339
$4_{32}-4_{23}$	23067.21	23067.224
$4_{23}-4_{14}$	22102.55	22102.569
$5_{32}-5_{23}$	16354.65	16354.668
$5_{23}-5_{14}$	14320.62	14320.609
$5_{14}-5_{05}$	23426.32	23426.338
$6_{33}-6_{24}$	15928.49	15928.488
$6_{24}-6_{15}$	19298.33	19298.354
$6_{15}-6_{06}$	30184.09	30184.082
$7_{43}-7_{34}$	22972.38	22972.356
$7_{34}-7_{25}$	17518.40	17518.384
$8_{44}-8_{35}$	21173.98	21173.984
$8_{35}-8_{26}$	21487.13	21487.113
$9_{45}-9_{36}$	21249.70	21249.713
	RMS Deviation	0.018 [b]

* Calculated with the help of rotational and centrifugal distortion parameters of Table III.

[a] Also confirmed by microwave—microwave double resonance experiments.

[b] The RMS deviation of a least square fit of the observed transition frequencies to a rigid rotor is 1.068 MHz.

spin weight intensity ratio depends upon the parity of the K_- K_+ labels and also upon the $\tilde{v}$ state. For the $\tilde{v}=1_1$ state rotational transitions, this comes out to be 66 : 176 : 64 : 72 for the ee ⟷ oo transitions and 55 : 176 : 64 : 56 for the eo ⟷ oe transitions. For the $\tilde{v}=1_2$ state rotational transitions it becomes 55 : 176 : 64 : 56 and 66 : 176 : 64 : 72 for the ee ⟷ oo and eo ⟷ oe transitions respectively[11, 12]. For the assignment of the first excited torsional state spectra we concentrated on the most abundant $(CD_3)_2{}^{80}Se$ species of the molecule and made an extensive search for them within ±150 MHz about the corresponding ground state $\tilde{v}=0_1$ line. In many cases we did observe the desired

Table II. Measured ground state rotational transitions of the $(CD_3)_2{}^{78}Se$ molecule. All frequencies are in MHz.

Transition $J_{K_-K_+}-J'_{K'_-K'_+}$	Observed frequency	Calculated frequency *
$1_{11}-0_{00}$	12452.31	12452.282
$2_{20}-2_{11}$	11100.55	11100.543
$2_{21}-2_{12}$	15679.09	15679.088
$2_{12}-1_{01}$	19678.08	19678.077
$2_{21}-1_{10}$	30130.66	30130.683
$3_{30}-3_{21}$	20113.32	20113.286
$3_{21}-3_{12}$	10611.83	10611.783
$3_{12}-3_{03}$	11243.82	11243.818
$3_{22}-3_{13}$	18467.81	18467.743
$3_{22}-2_{11}$	37356.55	37356.516
$3_{03}-2_{12}$	22709.89	22709.917
$4_{31}-4_{22}$	18310.92	18311.047
$4_{22}-4_{13}$	11509.78	11509.787
$4_{13}-4_{04}$	16801.16	16801.158
$4_{32}-4_{23}$	23299.96	23299.967
$4_{23}-4_{14}$	22200.37	22200.423
$5_{32}-5_{23}$	16624.71	16624.689
$5_{23}-5_{14}$	14317.49	14317.542
$5_{14}-5_{05}$	23379.70	23379.720
$6_{33}-6_{24}$	16113.08	16113.068
$6_{24}-6_{15}$	19207.39	19207.356
$6_{15}-6_{06}$	30148.08	30148.060
$7_{43}-7_{34}$	23422.85	23422.803
$7_{34}-7_{25}$	17573.71	17573.714
$8_{44}-8_{35}$	21528.98	21529.010
$8_{35}-8_{26}$	21390.92	21390.920
$9_{45}-9_{36}$	21433.31	21433.313
	RMS Deviation	0.039 [a]

* Calculated with the help of rotational and centrifugal distortion constants of Table III.

[a] The RMS deviation of a least square fit of the observed transition frequencies to a rigid rotor is 1.155 MHz.

Table III. Ground state parameters derived from the semi rigid rotor model according to Watson.

	$(CD_3)_2{}^{80}Se$	$(CD_3)_2{}^{78}Se$
A (MHz)	8782.406	8839.401
B (MHz)	5296.524	5296.497
C (MHz)	3603.330	3612.906
d_J (MHz)	−0.013994	−0.014600
d_{JK} (MHz)	−0.020536	−0.019581
d_K (MHz)	+0.055828	+0.059199
d_{WJ} (MHz)	+0.004288	+0.004367
d_{WK} (MHz)	−0.003326	−0.003695
I_a (amu Å^2)	57.56179	57.19064
I_b (amu Å^2)	95.44581	95.44629
I_c (amu Å^2)	140.2955	139.9237
$I_a+I_b-I_c$ (amu Å^2)	12.7121	12.7132
RMS Deviation [a] (MHz)	0.018	0.039

[a] The RMS deviation to a least square fit of the observed transition frequencies to a rigid rotor are 1.068 MHz and 1.155 MHz respectively.

triplets with the abovementioned characteristic intensity ratios and in some cases, their Stark lobes could also be recognized. However, the measured frequencies of the $A_1 A_2$ and $A_2 A_1$ components of the triplet did not fit into a rigid rotor pattern. This casted some doubt as to the correct assignment of the excited state spectrum. To confirm them, we made a number of successful microwave-microwave double resonance experiments. Thus by making six such double resonance experiments for both the $\tilde{v} = 1_1$ and 1_2 state spectra and using a number of convenient sum rules, we have been able to assign fourteen transitions for both of the first excited torsional state spectra. Of these only nine transitions showed measurable internal rotation splittings. The transitions of the torsional state $\tilde{v} = 1_1$ appeared to be stronger in intensity than those of the $\tilde{v} = 1_2$ state. The $[A_i A_j - (A_i E, E A_j)]$ splittings were different for the $\tilde{v} = 1_1$ and 1_2 state triplets.

Table IV presents the mean value of the measured internal rotation splittings in the $\tilde{v} = 1_1$ and 1_2 state spectra of the molecule. A computer program SPLIK. F 4 was available, which calculates the potential barrier V_3 and the angle α between one of the 'top axes' and the 'b axis' by making a least square fit to the observed average values[13] of the splittings $[A_i A_j - (A_i E, E A_j)]$. This program takes care of the second and fourth order perturbations and neglects the potential interaction parameters V_{12}' and V_{12}. The results are given in Table V.

Table IV. Observed and calculated internal rotation splitting of the transitions in the first excited torsional states of the $(CD_3)_2{}^{80}Se$ molecule [a].

Transition $J_{K_-K_+}-J'_{K'_-K'_+}$	Observed splitting [b]	Calculated splitting [c]	$\Delta\nu_{ob}-\Delta\nu_{cal}$
$2_{21}-2_{12}$	−1.74	−1.698	−0.042
$2_{21}-1_{10}$	−1.73	−1.693	−0.037
$2_{20}-1_{11}$	−2.00	−1.879	−0.121
$2_{20}-2_{11}$	−1.47	−1.271	−0.199
$3_{22}-2_{11}$	−1.42	−1.669	−0.249
$3_{22}-3_{13}$	−1.65	−1.922	+0.272
$4_{13}-4_{04}$	−1.37	−1.568	+0.198
$5_{14}-5_{05}$	−1.93	−2.183	+0.253
$6_{15}-6_{06}$	−3.25	−2.833	−0.417
		RMS Deviation	0.228

[a] All splittings are in MHz.

[b] Average of the observed $[A_i A_j - (A_i E, E A_j)]$ splitting in the 1_1 and 1_2 excited torsional state triplets of the transitions.

[c] Calculated with the help of the internal rotation parameters of Table V.

Table V. Internal rotation parameters.

	$(CD_3)_2{}^{80}Se$ [a]	$(CH_3)_2{}^{80}Se$ [b]
F (GHz)	86.05	166.1
s	87.05	42.12
$2 \cdot \alpha$ [c]	98° 20′	100° 7′
I_α (amu Å^2) [d]	6.35	3.244
V_3 (cal/mol)	1607	1500
Tilt of the top axis	1° 5′	1° 58′
∢ C Se C		96° 11′

[a] Present study, from the analysis of the internal rotation fine structure in the first excited torsional states of the molecule.

[b] Beecher's results (Ref. [7]), from the analysis of the ground state spectrum.

[c] For definition, see text.

[d] Kept constant at 6.35 amu Å^2, which is half of the observed inertia defect.

The corresponding values for the $(CH_3)_2{}^{80}Se$ molecule, as obtained by Beecher[7] from the analysis of the ground state spectrum are also given for comparison.

The publication of the detailed analysis of top-top coupling, including the determination of V_{12}' parameter is postponed as considerable computer time is necessary. Also, similar work on $(CH_3)_2{}^{80}Se$ is in progress.

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