Top-Top Interaction in Hexa-Deutero Dimethyl Selenide from the Microwave Spectrum in the First Excited Torsional States

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(Z. Naturforsch. **31 a**, 1413–1418 [1976]; received August 18, 1976)

An analysis of the internal rotation fine structure for the rotational transitions of hexa-deutero dimethyl selenide in the first excited torsional states is presented in terms of a molecular model with two degrees of freedom for the internal rotation or torsion of the two tops in addition to the three degrees of freedom for the overall rotation. By a least squares fit of the multiplet splittings of ten transitions in the $v_n=1_1$ and nine transitions in the $v_n=1_2$ excited torsional states, the following parameters have been obtained: $V_3=1493\pm9$ cal mol^{-1}; $\vartheta=50°\ 1'\pm7'$; $V_{12}'=28.4\pm0.3$ cal mol^{-1}. The splitting of the fine structure components could be nicely fitted, but not their absolute frequencies and the seperation between the two multiplets.

Introduction

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, we recently reported the microwave spectrum of hexa-deutero dimethyl selenide in the ground and first excited torsional states [1]. The ground state rotational lines were not found to split by the coupling between overall and internal rotation angular momenta. The first excited torsional state rotational transitions were found as two sets of triplets corresponding to $v_n=1_1$ and 1_2 states and their assignment was confirmed by Stark effect and microwave-microwave double resonance experiments [1]. Figure 1 gives the details of the microwave-microwave double resonance connections used in the assignment of the rotational transitions in the first excited torsional states of the molecule. In the previous publication [1], the internal rotation fine structure in the excited torsional states of the molecule was rather crudely analyzed. Only the average value of the multiplet splittings $[A_iA_j-(A_iE$ or $EA_j)]$ in the $v_n=1_1$ and 1_2 states were fitted to obtain the potential barrier V_3 and the angle ϑ between one of the top axes and the "b axis", while the top moment of inertia was held fixed and the top-top coupling parameters were neglected. In this publication, we present a more detailed analysis of the internal rotation fine structure of the first excited torsional state rotational transitions, which includes a possible determination of the top-top coupling parameter V_{12}' also.

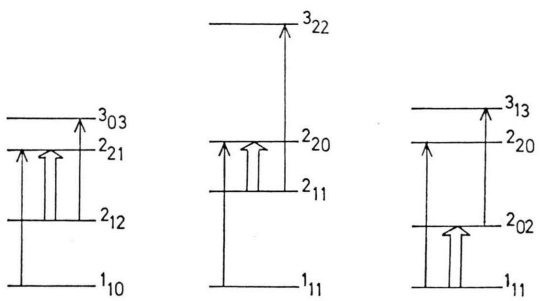

Fig. 1. Microwave-microwave double resonance connections used for the assignment of the rotational multiplets in the first excited torsional states.

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Theory and Method of Analysis

The analysis depends basically on a model in which the molecular frame and the methyl groups are assumed to be rigid. The two internal degrees of freedom are the internal rotations or torsions of the tops in addition to the three degrees of freedom for the overall rotation. The Hamiltonian operator for this molecular model is [2, 3]

$$H = A P_a^2 + B P_b^2 + C P_c^2 \qquad (1\,a)$$
$$+ F_1 \mathcal{P}_1^2 + F_2 \mathcal{P}_2^2 + F' (\mathcal{P}_1 \mathcal{P}_2 + \mathcal{P}_2 \mathcal{P}_1)$$
$$+ F_1 p_1^2 + (V_3/2)\,(1-\cos 3\,\alpha_1)$$
$$+ F_2 p_2^2 + (V_3/2)\,(1-\cos 3\,\alpha_2) \qquad (1\,b)$$
$$+ F' (p_1 p_2 + p_2 p_1) + V_{12} \cos 3\,\alpha_1 \cos 3\,\alpha_2$$
$$+ V_{12}' \sin 3\,\alpha_1 \sin 3\,\alpha_2 \qquad (1\,c)$$
$$- 2F' (p_1 \mathcal{P}_2 + p_2 \mathcal{P}_1) - 2F_1 p_1 \mathcal{P}_1 - 2F_2 p_2 \mathcal{P}_2 \qquad (1\,d)$$

where

$g = a, b, c$	the indices representing body fixed principle axes of inertia,
I_g	principle moment of inertia of the molecule,
$I_{ai}\,(i = 1, 2)$	moment of inertia of the top about their symmetry axes,
λ_{gi}	direction cosines between the ith top axis and the gth principle axes of inertia,
P_g	gth component of the total angular momentum,
p_i	angular momentum of the ith top about its symmetry axis,
p_i	$\sum_g \frac{\lambda g_i I_{ai} P_g}{I_g}$,
v_i	torsional quantum number of the ith top,
α_i	torsional angle of the ith top,
σ_i	symmetry index for the total eigenfunction,
V_3	barrier height,
V_{12} and V_{12}'	top-top coupling parameters.

$$F_i = \frac{\hbar}{4\pi} \frac{I_{ak}\left\{1 - \sum_g \frac{\lambda_g{}^2 I_{ak}}{I_g}\right\}}{I_{a_1} I_{a_2}\left\{1 - \sum_g \frac{\lambda_{g_1}{}^2 I_{a_1}}{I_g}\right\}\left\{1 - \sum_g \frac{\lambda_{g_2}{}^2 I_{a_2}}{I_g}\right\} - \left\{\sum_g \frac{\lambda_{g_1}\lambda_{g_2} I_{a_1} I_{a_2}}{I_g}\right\}^2}$$

with $k = \begin{cases} 2 \\ 1 \end{cases}$ for $i = \begin{cases} 1 \\ 2 \end{cases}$

$$F' = \frac{\hbar}{4\pi} \frac{I_{a_1} I_{a_2} \sum_g \frac{\lambda_{g_1}\lambda_{g_2}}{I_g}}{I_{a_1} I_{a_2}\left\{1 - \sum_g \frac{\lambda_{g_1}{}^2 I_{a_1}}{I_g}\right\}\left\{1 - \sum_g \frac{\lambda_{g_2}{}^2 I_{a_2}}{I_g}\right\} - \left\{\sum_g \frac{\lambda_{g_1}\lambda_{g_2} I_{a_1} I_{a_2}}{I_g}\right\}^2}.$$

The interpretation of the spectrum follows with a computer program in which the Hamiltonian operator is handled in the following way. In the first step, the matrix elements of the Hamiltonian (1 b) + (1 c) are set up in the basis of the eigenfunctions of (1 b), (a product of the Mathieu functions $U_{v_1\sigma_1}(\alpha_1)\, U_{v_2\sigma_2}(\alpha_2)$ of the two independent hindered rotors) and diagonalized to give the torsional energy eigenvalues and the eigenfunctions $\Phi_{\tilde{v}_n\sigma_n}$ *. The part (1 b) + (1 c) of the Hamiltonian describes a system of two hindered coupled tops with fixed axes. This matrix factors, when one uses symmetrized wave functions according to the irreducible representation of the group $C_{3v}^{-} \otimes C_{3v}^{+}$, whose symmetry operations leave the the total Hamiltonian (1) invariant. Because of the interaction through the part (1 c), the degeneracy of the levels $v_1 v_2 = 1, 0$ and 0, 1 is lifted.

In the second step, the wave functions $\Phi_{\tilde{v}_n\sigma_n}$ of the coupled internal rotors (as obtained in step 1) together with the Wang function $S_{J|K|\gamma M}$ are used as the basis for the total Hamiltonian (1). In this basis, the Hamiltonian is seen to be diagonal in J, M and σ_n, but neither in K nor in $\tilde{v}_n$. The matrix elements of (1 d) which connect states of different $\tilde{v}_n$ are treated by a Van Vleck transformation [4], correct to the second order.

In the third step, the resulting effective rotational Hamiltonian matrix is diagonalized and gives the eigenvalues of the operator (1).

A computer program MELITA was available which, based on the above mentioned procedure, calculates and/or fits the experimental splittings yielding values of the reduced barrier parameter s, the top-top coupling parameters V_{12}, V_{12}', the methyl top moment of inertia I_a, the orientation of the internal rotation axis in the principal axes system and the rotational constants.

Two important points should be mentioned. Firstly, on the convergence of the calculating pro-

* Henceforth, we use the notations of reference (3): $\tilde{v}_n$ to designate the torsional levels with $E_{\tilde{v}_n} \leqq E_{\tilde{v}_{n+1}}$, with $1 \leqq n \leqq \tilde{v}+1$. For example
$\tilde{v}_n = 0_1$ corresponds to $v_1 v_2 = 0\,0$,
$\tilde{v}_n = 1_1$ corresponds to $v_1 v_2 = 0\,1$,
$\tilde{v}_n = 1_2$ corresponds to $v_1 v_2 = 1\,0$ with $E_{1_1} \leqq E_{1_2}$,
and so on.

Table 1. Energy of torsional levels for Hexa-Deutero Dimethyl Selenide.

$\tilde{v}_n$	E_{tors} (in GHz)
0_1	3414
1_1	6706
1_2	6731
2_1	9788
2_2	9791
2_3	10029
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Table 2. Observed and calculated internal rotation splittings of the rotational transitions in the first excited torsional states of $(CD_3)_2{}^{80}Se$ molecule.

Transition $J_{K_-K_+} - J'_{K_-'K_+'}$	$\tilde{\nu}_n$	Species $\sigma_1\,\sigma_2$	Measured Frequency (MHz)	Measured Splitting * (MHz)	Calculated Splitting * (MHz)	Mean ** of the calculated EA and AE Splittings (MHz)	Deviation | measured − calculated | Splittings (MHz)
$1_{10}-2_{21}$	1_1	A_1A_2	29915.103				
		E E	29916.039	0.936	0.903		0.033
		A_1E	29916.920	1.817	1.872	1,807	0.010
		E A_2			1.742		
	1_2	A_2A_1	30003.713				
		E E	30004.531	0.818	0.822		0.004
		A_2E	30005.362	1.649	1.707	1.699	0.050
		E A_1			1.692		
$1_{11}-2_{20}$	1_1	A_1A_2	32108.360				
		E E	32109.429	1.069	1.062		0.007
		A_1E	32110.464	2.104	2.054	2.120	0.016
		E A_2			2.186		
	1_2	A_2A_1	32113.825				
		E E	32114.765	0.940	0.956		0.016
		A_2E	32115.716	1.891	1.855	1.911	0.020
		E A_1			1.967		
$1_{01}-2_{12}$	1_1	A_1A_2	19503.710				
		E E	19504.088	0.378	0.316		0.062
		A_1E	19504.358	0.648	0.632	0.631	0.017
		E A_2			0.630		
	1_2	A_2A_1	19683.740				
		E E	19684.011	0.270	0.253		0.017
		A_2E	19684.298	0.558	0.508	0.507	0.051
		E A_1			0.505		
$2_{12}-2_{21}$	1_1	A_1A_2	15620.022				
		E E	15620.940	0.918	0.895		0.023
		A_1E	15621.729	1.707	1.850	1.788	0.081
		E A_2			1.727		
	1_2	A_2A_1	15485.794				
		E E	15486.664	0.870	0.860		0.010
		A_2E	15487.562	1.768	1.777	1.722	0.046
		E A_1			1.667		
$2_{11}-2_{20}$	1_1	A_1A_2	10971.980				
		E E	10972.798	0.818	0.779		0.039
		A_1E	10973.623	1.643	1.492	1.556	0.087
		E A_2			1.619		
	1_2	A_2A_1	10998.589				
		E E	10999.236	0.647	0.714		0.067
		A_2E	10999.979	1.390	1.377	1.430	0.040
		E A_1			1.483		
$2_{11}-3_{22}$	1_1	A_1A_2	37052.281				
		E E	37053.259	0.978	0.957		0.021
		A_1E	37054.230	1.949	1.927	1.913	0.036
		E A_2			1.899		
	1_2	A_2A_1	37486.813				
		E E	37487.402	0.589	0.491		0.098
		A_2E	37487.710	0.897	0.995	0.983	0.086
		E A_1			0.972		
$3_{13}-3_{22}$	1_1	A_1A_2	18443.678				
		E E	18444.731	1.053	1.056		0.003
		A_1E	18445.797	2.119	2.121	2.109	0.010
		E A_2			2.096		
	1_2	A_2A_1	18404.507				
		E E	18405.179	0.672	0.715		0.043
		A_2E	18405.697	1.190	1.442	1.432	0.242
		E A_1			1.423		

Table 2 (cont.)

Transition $J_{K-K+} - J'_{K'-K'+}$	$\tilde{v}_n$	Species $\sigma_1 \sigma_2$	Measured Frequency (MHz)	Measured Splitting * (MHz)	Calculated Splitting * (MHz)	Mean ** of the calculated EA and AE Splittings (MHz)	Deviation | measured − calculated | Splittings (MHz)
$3_{12}-3_{21}$	1_1	A_1A_2	10450.729				
		E E	10451.593	0.864	0.816		0.048
		A_1E	10452.446	1.717	1.618	1.631	0.086
		E A_2			1.643		
	1_2	A_2A_1	***				
		E E	***		0.450		
		A_2E	***		0.895	0.902	
		E A_1	***		0.909		
$4_{04}-4_{13}$	1_1	A_1A_2	16992.821				
		E E	16993.575	0.754	0.751		0.003
		A_1E	16994.294	1.473	1.498	1.499	0.026
		E A_2			1.500		
	1_2	A_2A_1	16527.215				
		E E	16527.842	0.627	0.655		0.028
		A_2E	16528.474	1.259	1.309	1.313	0.054
		E A_1			1.318		
$5_{05}-5_{14}$	1_1	A_1A_2	23633.300				
		E E	23634.290	0.990	1.047		0.057
		A_1E	23635.304	2.004	2.089	2.091	0.087
		E A_2			2.093		
	1_2	A_2A_1	22994.074				
		E E	22994.976	0.902	0.952		0.050
		A_2E	22995.921	1.847	1.915	1.908	0.061
		E A_1			1.902		
					RMS deviation of the splittings		0.062

* Splittings with respect to the A_1A_2 or A_2A_1 species frequency.

** Arithmetic mean has been taken, as the relative intensity of the two components are approximately equal (theoretically) and calculated splittings between them are less than half the full width of the lines at half power points.

*** Not measured because of interfearing lines.

cedure in the first and the second step, it should be decided, what finite matrix out of the infinite one in $\tilde{v}_n$ is to be used. As has been concluded elsewhere also [3, 5], this could not be predicted in general and should be decided for the individual cases themselves. Figure 2 shows the dependence of the rotational eigenvalue of the level $J_\tau = 3_3$ ** on the maximum value of $\tilde{v}_n(v_{\max})$ used. In the case of torsional part as well as of rotational part, double precision was used, which means inclusion of 16 significant figures. It can be seen that the change of the eigenvalue of the 3_3 level from $v_{\max} = 7$ to 8 is much smaller than the accuracy of measurements, whereas that from $v_{\max} = 6$ to 7 is of the same order. In all the calculations, $v_{\max} = 8$ has been used.

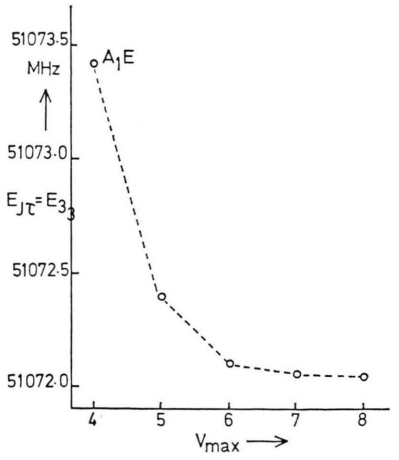

Fig. 2. Dependence of the rotational eigenvalue of the $J_\tau = 3_3$ level in the 1_1 excited torsional state (A_1E species) on the maximum torsional quantum number $v_{\max}$ used in the calculations.

** This level is among those in which the effect is most pronounced.

Secondly, in connection with the Van Vleck transformation, three versions of the program are available. a) Van Vleck transformation aiming at only one of the torsional levels at a time and without denominator correction [6, 7]; b) Van Vleck transformation aiming at only one of the torsional levels at a time and with denominator correction included; c) Van Vleck transformation aiming simultaneously at both of the nearly degenerate (for example $\tilde{v}_n = 1_1$ and 1_2) torsional states and without denominator correction. Table 1 gives the energy levels of the pure torsion. It could be seen that in the case of $(CD_3)_2{}^{80}Se$, the energy difference between the two torsional states of our interest, viz. $\tilde{v}_n = 1_1$ and 1_2 is of the same order as the rotational transition energies in a particular torsional state. Hence the Van Vleck transformation aiming simultaneously at both of the 1_1 and 1_2 states was used. With this, no need was realized to include the denominator correction, because the energy differences between these and other torsional states are at least two orders of magnitude larger than that between themselves.

It was found that the internal rotation splittings were not much sensitive to the variations of the rotational constants. Hence, their ground state values were used. Moreover, the parameters V_{12}, I_a and s proved to be so highly correlated that their simultaneous determination was not possible. Instead we have fixed $I_a = 6.35$ Å^2, which is half of the observed ground state inertia defect for the molecule and $V_{12} = 0$. The s, V_{12}' and ϑ were then determined by a least squares fitting procedure to the observed splittings of ten rotational transitions in the 1_1 and nine in the 1_2 excited torsional states. Table 2 gives the measured splittings and compares them to those calculated on the basis of the above procedure. Table 3 presents the correlation coefficients of the three internal rotation parameters fitted and Table 4 gives the root mean square partial derivatives of the splittings with respect to these parameters. Table 5 gives the final results.

Table 3. Correlation coefficients of the three fitted internal rotation parameters.

s	1.000		
ϑ	−0.658	1.000	
V'_{12}	0.364	−0.281	1.000

Table 4. Root mean square partial derivatives * of the various splittings (Table 2) with respect to the fitted internal rotation parameters.

$x = V_3$	7.1	kHz/cal mol^{-1}
$x = \vartheta$	496.2	kHz/degree
$x = V'_{12}$	196.8	kHz/cal mol^{-1}

* Defined as $\sqrt{\frac{1}{N}\sum_{i=1}^{N}\left\{\frac{\partial\, \Delta\nu_i}{\partial x}\right\}^2}$ for the N splittings with $x = V_3$, ϑ, V'_{12}.

Table 5. Internal rotation parameters.

s	79.2 ±0.5	
V_3	1493 ±9	cal mol^{-1}
V'_{12}	297 ±3	GHz
	28.4 ±0.3 §	cal mol^{-1}
V_{12}	0 *	GHz
I_a	6.35 §§	amu Å^2
ϑ	50° 1′ ± 7′	
F	87.847	GHz
F'	−3.605	GHz
A_x	3603.330 **	MHz
B_y	5296.524 **	MHz
C_z	8782.406 **	MHz

§ Conversion factor 1 GHz = 0.09536 cal mol^{-1}.
* Assumed arbitrarily.
§§ Kept fixed. This is half of the observed ground state inertia defect.
** Fixed at the ground state values (Reference 1).

It could be seen that all the deviations between the measured and calculated splittings are of the same order as the experimental uncertainties of the measured splittings, with the only exception of the $[A_2 E/E A_1 - A_2 A_1]$ splitting in the 1_2 multiplet of the transition $3_{13} - 3_{22}$. At present nothing can be said with certainty about this large deviation with the exception that in our rather cruder analysis of the previous publication [1], this transition was among those in which largest fourth order contribution to the splittings was seen. This could partially be the reason, because the present calculation does not include the fourth order contribution to the splittings. The angle ϑ, as obtained in this work is within the experimental uncertainty to that obtained by Beecher [8] from the ground state work of the normal species of the molecule. The same is true for the potential barrier parameter V_3. The top-top coupling parameter V_{12}' is about 2% of V_3. This is of the same order as obtained for the other molecules of this series (0.53% for dimethyl ether [9]; 1.6% for dimethyl sulphide [3]).

Acknowledgements

We are thankful to Prof. Dr. H. D. Rudolph and Dr. B. Tan for supplying the revised version of his MELITA program. Thanks are also due to the Rechenzentrum der Universität Kiel, where all the calculations have been done as also to the Computer Center of Hamburg University, where parts of the program were run and tested. The financial support by the Deutsche Forschungsgemeinschaft and the Fonds der Chemie is also thankfull acknowledged. One of us (GKP) is also thankful to the Alexander-von-Humboldt Foundation, Germany for the award of a post-doctoral Fellowship.

[1] G. K. Pandey and H. Dreizler, Z. Naturforsch. **31 a**, 357 [1976].
[2] L. Pierce, J. Chem. Phys. **34**, 498 [1961].
[3] A. Trinkaus, H. Dreizler, and H. D. Rudolph, Z. Naturforsch. **28 a**, 750 [1973].
[4] E. C. Kemble, Fundamental Principles of Quantum Mechanics, McGraw-Hill Book Company, Inc., New York 1937.
[5] H. Dreizler and H. Legell, Z. Naturforsch. **28 a**, 1414 [1973].
[6] D. R. Herschbach, J. Chem. Phys. **31**, 91 [1959]; H. Dreizler, Forsch. Chem. Forsch. **10**, 59 [1968].
[7] D. Stelman, J. Chem. Phys. **41**, 2111 [1964].
[8] J. F. Beecher, J. Mol. Spectroscopy **4**, 414 [1966].
[9] H. Lutz and H. Dreizler, Z. Naturforsch. **31 a**, 1026 [1976].