Evidence of Tilt of the Methyl Top Axis in the r_s-structure of Dimethyl Selenide

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The complete r_s-structure of dimethyl selenide has been determined by using suitably chosen changes in principal moments of inertia of a number of isotopic species. The tilt of the methyl top axis with respect to the C–Se bond, as determined by the analysis of the internal rotation fine structure of the rotational transitions is also evidenced in the r_s-structure. The center of mass condition has been used.

In order to fit the internal rotation splittings in the rotational spectra of the molecules dimethyl ether [1, 2], dimethyl sulphide [3, 4], dimethyl selenide [5] of the series $(CH_3)_2-X$, with X a group VI atom, it was found necessary to assume the symmetry axis of the methyl top to be tilted by few degrees with respect to the corresponding X–C bond. For the former two molecules, the tilt was also confirmed by determining the r_s-coordinates of the hydrogen atoms with suitable isotopic substitutions in the molecule. For the latter case, viz. dimethyl selenide, this could not be done [5] because of the insufficient number of available isotopic substitutions for the hydrogen atoms. Beecher [5], using a mixed r_s, r_0-procedure calculated the coordinates of the six hydrogen atoms with tilt (as obtained by his analysis of the internal rotation fine structure) or without tilt.

As we have recently measured the rotational constants of two more deuterated samples of the molecule [6], it is now possible to work out the complete r_s-structure of the molecule by a procedure specially adopted to this type of molecules and substitution. We have undertaken this work with the interest to see if the tilt of the methyl top axis, as obtained by the analysis of the internal rotation splittings [5, 6] could be confirmed in the r_s-structure also.

The rotational constants and moments of inertia used are given in Table 1. The b-coordinate of the selenium atom and the a- and b-coordinates of the carbon atoms were calculated by the substitution method, using the changes in moments of inertia between $(CH_3)_2{}^{80}Se$ and $(CH_3)_2{}^{78}Se$, and $(CH_3)_2{}^{80}Se$ and $^{13}CH_3-{}^{80}Se-CH_3$ molecules respectively with the help of Eqs. (13.71) – (13.74) of Reference [7]. This was also done by Beecher [5]. The calculation of the hydrogen coordinates $(\pm a_1, b_1, 0)$ for the symmetric and $(\pm a_2, b_2, \pm c_2)$ for the asymmetric hydrogen atoms could not be done in the conventional ways [8, 9], because rotational constants for the singly deuterated species are not yet measured.

In what follows we describe a method, which can be used to determine the hydrogen coordinates in a molecule containing two equivalent methyl groups [such as $(CH_3)_2-X$] by using only changes in the principle moment of inertia between normal and hexadeuterated and normal and trideuterated species of the molecule. We experienced, that the monodeuterated species of a molecule is, in general, costlier to prepare and its spectrum is also sometimes more difficult to interpreat.

In going from the normal (6H) to the hexadeuterated (6D) species of the molecule, it can be stated that the C_{2v} symmetry axis and the symmetry plane of the molecule remain unchanged, only the origin is shifted along the b-axis. One has

$$\begin{aligned} I_a(6D) - I_a(6H) &= 2\,\Delta m\,(b_1^2 + 2\,b_2^2) \\ &\quad + 4\,\Delta m\,c_2^2 - 4\,\mu_6\,t^2\,, \\ I_b(6D) - I_b(6H) &= 2\,\Delta m\,(a_1^2 + 2\,a_2^2) \\ &\quad + 4\,\Delta m\,c_2^2\,, \qquad (1) \\ I_c(6D) - I_c(6H) &= 2\,\Delta m\,(a_1^2 + 2\,a_2^2) \\ &\quad + 2\,\Delta m\,(b_1^2 + 2\,b_2^2) - 4\,\mu_6\,t^2\,. \end{aligned}$$

where

$$\begin{aligned} \Delta m &= m_D - m_H\,, \\ \mu_6 &= \frac{(\Delta m)^2}{M + 6\,\Delta m}\,, \\ t &= b_1 + 2\,b_2\,. \qquad (2) \end{aligned}$$

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Table 1. The rotational constants and moments of inertia of the different isotopic species of dimethyl selenide used for working out the r_s-structure.

	$(CH_3)_2{}^{80}Se$ [a]	$(CH_3)_2{}^{78}Se$ [a]	$^{13}CH_3{}^{80}SeCH_3$ [a]	$CD_3{}^{80}SeCH_3$ [a]	$(CD_3)_2{}^{80}Se$ [b]
A (MHz)	11300.43	11369.93	11102.19	10013.31	8782.406
B (MHz)	6912.83	6912.76	6715.73	5960.13	5296.524
C (MHz)	4528.79	4539.91	4412.19	4017.77	3603.330
I_a (amu Å^2) [c]	44.73555	44.46210	45.53435	50.48590	57.56179
I_b (amu Å^2) [c]	73.12938	73.13012	75.27566	84.81879	95.44581
I_c (amu Å^2) [c]	111.62606	111.35264	114.57598	125.82377	140.29550

[a] J. F. Beecher, Reference 5.
[b] G. K. Pandey and H. Dreizler, Reference 6.
[c] Conversion factor $5.05531 \cdot 10^5$ MHz·amu Å^2; mass scale ^{16}O.

From these equations one can readily get

$$c_2^2 = \frac{P_c(6D) - P_c(6H)}{4\,\Delta m} \tag{3}$$

$$a_1^2 + 2\,a_2^2 = \frac{P_a(6D) - P_a(6H)}{2\,\Delta m} \tag{4}$$

$$b_1^2 + 2\,b_2^2 = \frac{P_b(6D) - P_b(6H)}{2\,\Delta m} + \frac{2\,\mu_6\,t^2}{\Delta m} \tag{5}$$

where

$$P_a = \tfrac{1}{2} \cdot (-I_a + I_b + I_c)$$

with cyclic permutation for P_b and P_c.

Also in going from the normal to the 3 deuterated species $(CD_3 - X - CH_3)$ of the molecule the plane of the symmetry remains but the C_{2v} symmetry of the molecule is destroyed. Thus again one can show that

$$I_c(3D\,3H) - I_c(6H) = \Delta m\,(b_1^2 + 2\,b_2^2) + \Delta m\,(a_1^2 + 2\,a_2^2) - \mu_3\,t^2 - \mu_3\,(a_1 + 2\,a_2)^2 \tag{6}$$

with $$\mu_3 = (\Delta m)^2/(M + 3\,\Delta m)\ .$$

Inserting Eqs. (3), (4) and (5) in Eq. (6) one gets

$$|a_1 + 2\,a_2| = \left| \left\{ \frac{P_b(6D) - P_b(6H)}{2\,\mu_3} + \frac{2\,\mu_6\,t^2}{\mu_3} - t^2 + \frac{P_a(6D) - P_a(6H)}{2\,\mu_3} - \frac{I_c(3D\,3H) - I_c(6H)}{\mu_3} \right\}^{1/2} \right| . \tag{7}$$

t in Eq. (2) can be calculated from the known b-coordinates of the X and C atoms and using the center of mass condition for the parent $(CH_3)_2 - X$ molecule. The values of b_1 and b_2 can then be determined by solving Eq. (2) and (5) and of a_1 and a_2 by solving Eqs. (4) and (7)*.

* As the solution involves a quadratic equation one gets two sets of values for b_1 and b_2, corresponding to which four sets of values for a_1 and a_2 are obtained. The correct set is chosen on the basis of plausability and a comparison with the r_0-structure.

In order to check the validity of this method, we first tried it on dimethyl ether, where sufficient experimental data are available to evaluate the hydrogen coordinates from singly deuterated species data employing normal substitution method and also by the proposed method. We found general agreement (within experimental uncertainty) between the two sets of calculated coordinates.

The results of the calculation for dimethyl selenide are given in Table 2. Some checks can be made on these calculated r_s-coordinates. In the above calculations $I_a(3D\,3H) - I_a(6H)$ and $I_b(3D\,3H) - I_b(6H)$ have not been used, so they can be used as independent checks on the calculated structure. Also the experimental data for $(CD_3)_2{}^{78}Se$ and $CD_3 - {}^{78}Se - CH_3$ are available and can be used as checks. For these the calculated ΔI's were found to differ at the worst by 0.008 amu Å^2 from the corresponding experimental data (Table 3). This shows the correctness of the determined structure. The reason for such a consistancy could be that none of the atoms lied very near to any of the principle coordinate axis, making thereby the structure determination to be less contaminated by the zero point vibrational effects.

Table 2. The r_s-coordinates of dimethyl selenide in the principle axis system of $(CH_3)_2{}^{80}Se$. Center of mass condition used for b-coordinates, see text.

	a	b	c
Se	0.0 *	−0.3667	0.0 *
C	±1.4490	+0.9309	0.0 *
H_s	±2.3595	+0.3360	0.0 *
H_a	±1.3982	+1.5584	±0.8970

* Assumed by symmetry.

Table 3. Comparison between calculated and observed changes in moments of inertia, which are not used in the structure determination of Table 2 and Table 4.

	Observed (amu Å²)	Calculated (amu Å²)
$I_a[CH_3{}^{80}SeCD_3] - I_a[(CH_3)_2{}^{80}Se]$	5.75035	5.75305
$I_b[CH_3{}^{80}SeCD_3] - I_b[(CH_3)_2{}^{80}Se]$	11.6894	11.6840
$I_a[(CD_3)_2{}^{78}Se] - I_a[(CH_3)_2{}^{80}Se]$	12.4551	12.4587
$I_b[(CD_3)_2{}^{78}Se] - I_b[(CH_3)_2{}^{80}Se]$	22.3169	22.3191
$I_c[(CD_3)_2{}^{78}Se] - I_c[(CH_3)_2{}^{80}Se]$	28.2976	28.2992
$I_a[CH_3{}^{78}SeCD_3] - I_a[(CH_3)_2{}^{80}Se]$	5.44835	5.44951
$I_b[CH_3{}^{78}SeCD_3] - I_b[(CH_3)_2{}^{80}Se]$	11.6709	11.6617
$I_c[CH_3{}^{78}SeCD_3] - I_c[(CH_3)_2{}^{80}Se]$	13.8719	13.8719

Table 4. Structural parameters derived from the r_s-coordinates of Table 2. Errors in brackets. Derived from the uncertainties of the rotational constants.

r(Se−C) *	1.945 (0.4) Å
r(C−H_s)	1.088 (13) Å
r(C−H_a)	1.096 (4) Å
∠ C−Se−C *	96° 19′ (5′)
∠ Se−C−H_s	105° 0′ (40′)
∠ Se−C−H_a	110° 20′ (15′)
∠ H_a−C−H_a	109° 52′ (30′)
∠ H_a−C−H_s	110° 37′ (30′)
∠ $2\cdot\Theta$	101° 34′ (1° 40′)
angle of tilt	2° 38′ (50′)

* Also determined by Beecher, Reference 5.

Table 4 presents the structural parameters of the molecule as derived from the coordinates of Table 2. The interesting feature of the structure concerns the methyl group. First, the methyl groups are found to be somewhat asymmetric, the angles $H_a - C - H_a$ and $H_a - C - H_s$ differ by 44′, which is more than twice the estimated uncertainty of 20′ for the angles. (This estimated uncertainty allows the zero point contribution of 0.01 amu Å² to the ΔI's for replacement of H by D.) Secondly, the methyl groups do not have their symmetry axes coincident with the C − Se bond direction but are tilted by 2° 38′, which makes the angle between the symmetry axes 5° 16′ larger than the C − Se − C angle. This angle of tilt agrees both in magnitude and sign with the tilt angle of 1° 58′ obtained by the analysis of the internal rotation splittings of the lines [5, 10].

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