Investigation of the Internal Rotation in Propargyl Mercaptan by Microwave Spectrum Analysis

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The microwave investigation of propargyl mercaptan has been continued to study the internal rotation of the SH group in the molecule. A Hamiltonian is proposed to describe the over-all rotation and the torsion of the top. The analysis leads to the result that the potential function is a double minimum potential with a lower barrier of 470 ± 10 cm^{-1} at the cis position and a higher barrier of 2000 ± 500 cm^{-1} at the trans position.

Introduction

The microwave spectrum of propargyl mercaptan, Fig. 1, was shown by BOLTON and SHERIDAN[1] to correspond to the gauche configuration, Fig. 2. A striking series of μ_c-lines were analysed as rotation-vibration transitions between the two lowest states of the SH-torsion mode, and the separartion of these two vibrational levels was shown, with accuracy, to be only some 6890 MHz. In consequence, the μ_a- and μ_b-transitions appeared as close doublets of equal intensity, and, although, in the tabulation of the data, assignment of certain members of these doublets to one or other of the two vibrational states could be tentatively made, and sometimes deduced with certainty, a detailed analysis of the doublets was deferred, pending an accurate treatment of the perturbations between the energy level manifolds of the two states, the effects of which were obvious for certain transitions. BOLTON and BARON (private communication, to be separately published) have refined considerably the treatment of the perturbations, and have been kind enough to provide us with details of these computations.

In the present work, we report the first measurements of the lowest rotational transitions, from which a very accurate value of Δ, the energy between the ground level and the first torsional leve, is derived, and we have made a preliminary determination of dipole moment components from Stark effects. The spectrum of the deuterated species, $HCCCH_2SD$, is also assigned, allowing a closer estimate of the equilibrium dihedral angle of the SH-group, and we propose a potential function for the SH-torsion on the basis of refined measurements of a number of transitions.

Experimental

The spectra have been recorded in the region from 5 to 40 GHz with a Stark modulation microwave spektrograph, employing phase stabilized BWO's as radiation sources [2, 3]. The radio frequency microwave double resonance (RFMDR) technique was applied in the way described elsewhere [4, 5, 6].

First we have analyzed the spectrum of the deuterated species, $HCCCH_2SD$ (it will be called the "D-species"). The deuteration was carried out directly in

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[6] R. SCHWARZ, unpublished results.

the absorption cell at a temperature of about –60 °C. By using the RFMDR technique the μ_a-spectrum was assigned and the B and C rotational constants evaluated, Tab. 1. The μ_b-spectrum was not found, probably because of the weakness of the lines due to the small dipole moment component and to the incomplete deuteration. The measured lines did not show any internal rotation splitting, indicating that the separation between the ground and the first torsional level is less than in the case of the H-species.

Table 1. Observed and calculated μ_a-transitions of $HCCCH_2SD$ in MHz. Rotational constants in MHz. The frequencies were calculated using a rigid rotor procedure.

Transition	Observed frequency	Calculated frequency
$3_{12} \leftarrow 2_{11}$	17 610.664	17 610.664
$4_{22} \leftarrow 3_{21}$	22 953.946	22 955.127
$4_{04} \leftarrow 3_{03}$	22 888.695	22 889.383
$4_{31} \leftarrow 3_{30}$	22 931.417	22 930.512
$4_{32} \leftarrow 3_{31}$	22 931.417	22 930.355
$4_{23} \leftarrow 3_{22}$	22 920.826	22 920.923

$A^* = --$; $B = 3\,005.5 \pm 0.2$; $C = 2\,725.4 \pm 0.2$.

* The value of the A rotational constant obtained from the strucure fitting was A = 20 349 MHz.

The measurement of the $0_{00} \rightarrow 1_{01}$ transition for the H-species, which was missing in the previous work because of its low frequency, allowed us to calculate exactly the splitting for the H-species between the ground and the first torsional level: $\Delta = 6891.76 \pm 0.02$ MHz.

In this work some additional transitions of the H-species have been measured making use of the RFMDR whenever possible. Furthermore other transitions were remeasured in order to resolve the doublets, which had not been previously resolved, or possibly to improve the frequency measurements, Table 3.

From the Stark effect of some low J lines and using a simple rigid rotor treatment, we obtained preliminary results for the in-plane dipole moment components of the H-species: $\mu_a = 0.74 \pm 0.02$ D, $\mu_b = 0.58 \pm 0.01$ D. These values are averaged between the ground and the first torsional level and the errors are defined within the procedure used. A thorough treatment taking into account both the rotation and the torsion is in progress.

With the rotational constants of the H- and D-species, assuming the acetylene structure [7], a structure fitting was made and the internal rotation angle corresponding to the gauche position was evaluated to be: $\alpha_{min} = 127° \pm 1°$ (measured from the trans position). The A rotational constant given in Table 1 results also from this structure.

[7] "Tables of Interatomic Distances and Configuration in Molecules and Ions". The Chemical Society, London 1965.

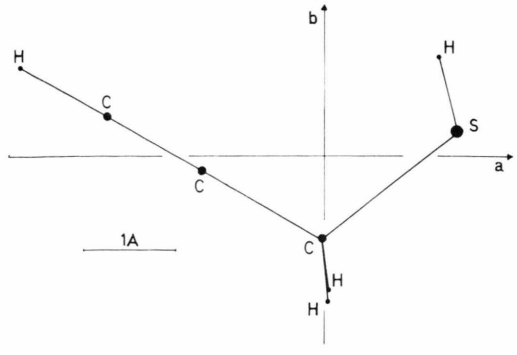

Fig. 1. Propargyl mercaptan in the a-b plane.

The spectrum of the trans rotamer, Fig. 2, was also searched for at different temperatures, but no evidence of this form was found.

Hamiltonian for the Rotation and the Internal Rotation

Following the same approximation that HIROTA used in the case of propargyl alcohol [8], we have treated the SH group as a symmetric top rotating about the C-S bond. The justification for this approximation is that the framework is heavy compared to the top.

The Hamiltonian that we have used is the following:

$$\mathcal{H} = H_R + H_T + H_{RT} \tag{1}$$

with

$$H_R = A^0 P_a^2 + B^0 P_b^2 + C^0 P_c^2 + F(\varrho_a^2 P_a^2 + \varrho_b^2 P_b^2) + F\varrho_a\varrho_b(P_a P_b + P_b P_a),$$

$$H_T = F p_\alpha^2 + \tfrac{1}{2}V_1(1 - \cos\alpha) + \tfrac{1}{2}V_2(1 - \cos 2\alpha) + \tfrac{1}{2}V_3(1 - \cos 3\alpha)$$

$$H_{RT} = -2F p_\alpha(\varrho_a P_a + \varrho_b P_b)$$

in which H_R is the rotational part, H_T the torsional part, H_{RT} the rotation-torsion interaction part; A^0, etc. are rotational constants; $\varrho_a = \lambda_a I_\alpha / I_a$, etc.; λ_a, etc. are the direction cosines between the internal rotation axis and the principal axes of the entire molecule; I_α is the moment inertia of the top about the internal

[8] E. HIROTA, J. Mol. Spectrosc. 26, 335 [1968].

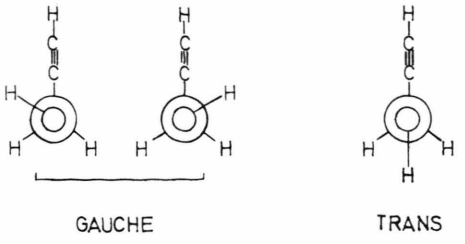

Fig. 2. Gauche and trans rotamers of propargyl mercaptan.

rotation axis; F is the inverse reduced moment of inertia of the top; and $p_\alpha = -i\,\partial/\partial\alpha$.

At this point, by simple consideration based on group theory, it is possible to explain the selection rules governing the pure rotation transitions and the torsion-rotation transitions of this molecule. The Hamiltonian (1) belongs to the invariance group C_i, which is a subgroup of the direct product $C_s \otimes V$. The group C_i has the following character table:

C_i	E	i
A_+	1	1
A_-	1	−1

with the generating elements [9] (I^r representation)

$$\text{E:} \quad \alpha \rightrightarrows \alpha,\ \varphi \rightrightarrows \varphi,\ \vartheta \rightrightarrows \vartheta,\ \chi \to \chi,\ p_\alpha \to p_\alpha,\ P_a \rightrightarrows P_a,\ P_b \to P_b,\ P_c \to P_c$$

$$\text{i} = \sigma_h C_{2c}\text{:} \quad \alpha \to -\alpha,\ \varphi \to \varphi + \pi,\ \vartheta \to \pi - \vartheta,\ \chi \to -\chi,\ p_\alpha \to -p_\alpha,\ P_a \to -P_a,\ P_b \to -P_b,\ P_c \to P_c$$

The dipole moment components all belong to the A_- symmetry species. The eigenfunctions of the Hamiltonian (1) must belong either to A_+ or A_-. They are linear combinations of the product of the torsional functions, $U_{v\pm}(\alpha)$, and the asymmetric rotor functions $\psi_{JK_{-1}K_{+1}M}$. The torsional functions $U_{v\pm}(\alpha)$ can be easily specified under the group C_i, the + and − signs characterizieg the symmetry of the torsional levels v according to A_+ and A_-, respectively. The rotational functions $\psi_{JK_{-1}K_{+1}M}$, which are usually specified under the group V, can be correlated to the species of the group C_i by the following correlation table:

C_i	V	$K_{-1}K_{+1}$
A_+	A	ee
	B_c	oe
A_-	B_b	oo
	B_a	eo

Figure 3 indicates the species of some ro-torsional levels of $HCCCH_2SH$ as they follow from the above considerations (A_+ and A_- being replaced by + and −, respectively, as it will be done later on).

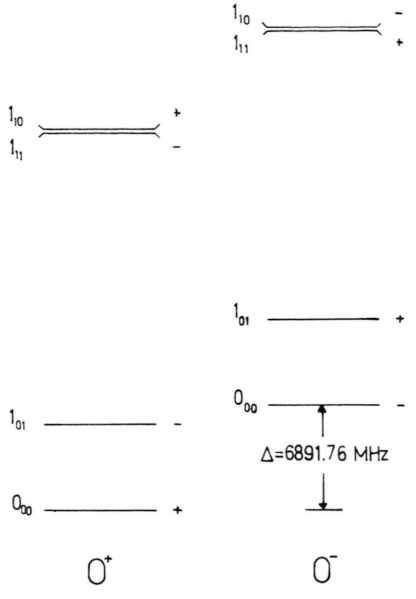

Fig. 3. Energy level pattern for the ground state (0+) and for the first torsional state (0−) of $HCCCH_2SH$. The symmetry of the ro-torsional levels according to the species of group C_i is shown by + and − corresponding to A_+ and A_-.

For the transition moment to be non-vanishing the selection rules are:

$$- \longleftrightarrow + \quad ; \quad \pm \not\leftrightarrow \pm$$

Now it is straightforward to see that the μ_a and μ_b transitions can only connect ro-torsional levels of the same torsional species and, therefore, in the microwave region, they are pure rotation transitions. On

[9] H. Dreizler, Fortsch. Chem. Forsch. 10, 59 [1968].

the other hand the μ_c transitions can only connect rotorsional levels of different torsional species and, therefore, they are torsion-rotation transitions.

Solution of the Hamiltonian

The sequence of our calculations was the following. First the matrix corresponding to the Hamiltonian H_T was set up in the free rotor functions: $(2\pi)^{-\frac{1}{2}} \exp(ima)$. The diagonalization of this matrix yielded the torsional eigenfunctions $U_{v\pm}(\alpha)$. The matrix corresponding to the total Hamiltonian (1) was then set up in the product basis: $U_{v\pm} \cdot \psi^{\times}_{JKM}$, where the symmetric rotor functions, $\psi^{\times}_{JKM}$, were chosen for simplicity instead of the asymmetric rotor functions, $\psi_{JK_{-1}K_{+1}M}$. This matrix was diagonalized using that set of rotational constants, A^0, B^0, C^0, which best reproduced the absolute frequencies of the lines listed in Table 3. The heights of the cis and trans barrier, V_{cis} and V_{trans}, were calculated by least squares fitting the experimental splitting Δ and the splittings of the lines, Table 3.

At this point we realized that a better fitting of the line splitting could be obtained using two slightly different sets of rotational constants, $A^0 + \Delta A^0$, etc., and $A^0 - \Delta A^0$, etc. for the + and − torsional levels, respectively. This treatment can be thought of as a first order approximation to the dependence of the rotational constants on the torsion.

A final least squares fit was made using the increments of the rotational constants, ΔA^0, ΔB^0, ΔC^0, as fitting parameters.

Table 2 gives all the constants that enter into the Hamiltonian (1) and the heights of the cis and trans

Table 2. Values of the constants which enter into the Hamiltonian (1). A°, B°, C°, ΔA°, ΔB°, ΔC° are in MHz; F, V_1, V_2, V_3 are in cm^{-1}; α_{min} is in degrees. Values of V_{cis} and V_{trans} are in cm^{-1}.

A°	=	22 346.70
B°	=	3 046.50
C°	=	2 756.50
ΔA°	=	0.722
ΔB°	=	−0.108
ΔB°	=	−0.026
F	=	9.115
α_{min}	=	$127^\circ \pm 1^\circ$
V_1	=	−2 071
V_2	=	−564
V_3	=	540
V_{cis}	=	470 ± 10
V_{trans}	=	2 000 ± 500

Table 3. Observed and calculated frequencies in MHz for the 0^+ and 0^- torsional states of $HCCCH_2SH$. Observed and calculated splittings in MHz. The calculations are based on the Hamiltonian (1) and on the constants given in Tab. 2. For the calculated frequencies the centrifugal distortion was not taken into account.

Transition	0^-		0^+		Obs. Splitting ($\nu_{0^+} - \nu_{0^-}$)	Calc. Splitting ($\nu_{0^+} - \nu_{0^-}$)
	Observed frequency	Calculated frequency	Observed frequency	Calculated frequency		
$1_{01} \leftarrow 0_{00}$	5 803.180	5 803.134	5 802.829	5 802.713	0.351	0.421
$1_{11} \leftarrow 0_{00}$	25 104.853	25 105.010	25 103.544	25 103.679	1.309	1.331
$1_{10} \leftarrow 1_{01}$	19 589.860	19 589.970	19 588.750	19 588.521	1.110	1.449
$2_{11} \leftarrow 1_{10}$	11 894.976	11 894.226	11 893.944	11 893.658	1.032	0.568
$2_{12} \leftarrow 1_{11}$	11 317.920	11 318.146	11 318.220	11 318.645	−0.300	−0.499
$2_{02} \leftarrow 1_{01}$	11 603.184	11 603.031	11 602.272	11 602.201	0.912	0.830
$2_{12} \leftarrow 1_{01}$	30 619.893	30 620.023	30 618.498	30 619.611	1.395	0.412
$2_{11} \leftarrow 2_{02}$	19 881.740	19 881.166	19 880.540	19 879.978	1.200	1.188
$3_{21} \leftarrow 2_{20}$	17 423.489	17 422.466	17 422.251	17 421.377	1.238	1.089
$3_{22} \leftarrow 2_{21}$	17 410.731	17 409.881	17 409.489	17 408.791	1.242	1.090
$3_{12} \leftarrow 2_{11}$	17 838.834	17 838.196	17 840.139	17 838.899	−1.305	−0.703
$3_{03} \leftarrow 2_{02}$	17 396.655	17 396.456	17 395.395	17 395.239	1.260	1.217
$3_{13} \leftarrow 2_{02}$	35 992.663	35 991.737	35 995.309	35 994.435	−2.646	−2.698
$3_{12} \leftarrow 3_{03}$	20 324.019	20 322.905	20 325.100	20 323.638	−1.081	−0.733
$4_{22} \leftarrow 3_{21}$	23 243.592	23 242.332	23 241.864	23 178.613	1.728	1.484
$4_{23} \leftarrow 3_{22}$	23 211.636	23 210.888	23 210.040	23 240.848	1.596	1.467
$4_{04} \leftarrow 3_{03}$	23 180.376	23 180.189	23 178.780	23 209.421	1.596	1.576
$4_{13} \leftarrow 4_{04}$	20 920.314	20 919.802	20 927.538	20 926.998	−7.224	−7.196
$5_{05} \leftarrow 4_{04}$	28 951.208	28 951.048	28 949.236	28 949.146	1.972	1.902
$6_{33} \leftarrow 5_{32}$	34 841.238	34 857.794	34 840.133	34 834.473	1.105	2.231
$6_{34} \leftarrow 5_{33}$	34 838.754	34 836.611	34 837.667	34 703.747	1.087	2.138
$6_{06} \leftarrow 5_{05}$	34 705.942	34 705.943	34 703.737	34 835.563	2.205	2.196

barriers. Table 3 gives the observed and calculated values of the frequencies and of the splittings of the μ_a and μ_b-lines for the H-species. Table 4 gives the rotational constants of the H-species corresponding to the ground (0^+) and to the first torsional level (0^-), as obtained from the low J transitions.

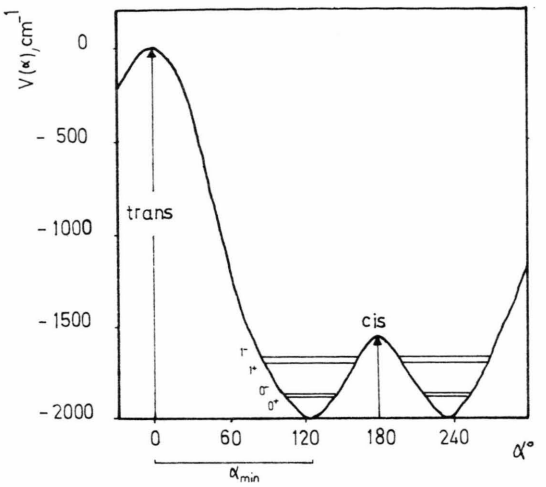

Fig. 4. Potential function for the internal rotation in propargyl mercaptan. The torsional levels 0^+, 0^-, 1^+, 1^- for the H-species are indicated.

Discussion

The potential function, as shown in Fig. 4, is a double minimum potential and the internal rotation splitting Δ is due to tunnelling of the two gauche forms through the cis barrier. This explains why the splitting Δ and consequently the splittings of the lines are much more sensitive to the cis barrier than to the trans barrier, and why the trans barrier remains rather undetermined.

Table 4. Rotational constants in MHz and asymmetry parameter for the 0^+ and 0^- states of $HCCCH_2SH$, by using a rigid rotor fitting procedure.

	0^+	0^-
A	22 347.56 ± 0.05	22 346.39 ± 0.05
B	3 045.80 ± 0.03	3 045.47 ± 0.03
C	2 757.39 ± 0.03	2 757.37 ± 0.03
$\varkappa$	−0.97055	−0.97059

The results shown in Tab. 3 indicate a reasonable agreement between the experimental splittings of the lines and those calculated using the Hamiltonian (1). This allows us to say with confidence that the simplified Hamiltonian (1) is a good one for studying the internal rotation in propargyl mercaptan. It could as well be used for studying other similar molecules.

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