

## Centrifugal distortion analysis of the microwave spectrum of allyl isothiocyanate (C-gauche conformer)

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**Abstract.** The ground state microwave rotational spectrum of the C-gauche conformer of allyl isothiocyanate has been reinvestigated by extending the frequency range up to 37.0 GHz. A detailed centrifugal distortion analysis has been carried out with previously reported and newly assigned microwave rotational transition frequencies. The evaluated rotational and centrifugal distortion constants are presented.

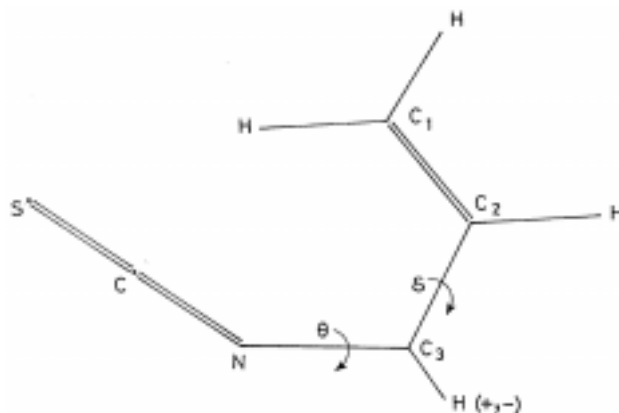
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### 1. Introduction

The observed microwave rotational transition frequencies of an asymmetric top molecule can be explained by rigid rotor approximation. According to this approximation, the molecular framework is assumed to be rigid. However, in reality, this is not the case. The bond distances and bond angles vary due to the centrifugal force produced by rotation. As a result, the molecule takes up a centrifugally distorted configuration instead of staying in an equilibrium configuration. Hence, the microwave rotational spectra can no longer be explained by a set of three rotational constants alone and the effect of centrifugal distortion (CD) on the rotational energy levels of the molecule has to be considered. This effect becomes much more pronounced in case of lighter molecules and in higher rotational states.

In an earlier paper [1] we have reported an analysis of the microwave spectrum of allyl isothiocyanate ( $\text{H}_2\text{C}=\text{CHCH}_2\text{NCS}$ ) in the frequency range 12.4–26.0 GHz. From this analysis of *a*-type *R*-branch transitions, it was concluded that in the vapour phase, allyl isothiocyanate predominantly exists in the C-gauche conformation having NCS group *cis* with respect to the C–C bond. This conclusion was found to be quite consistent with the results obtained with other allyl compounds [2–5]. The geometry of the molecule is shown in figure 1. Only *a*-type transitions ( $\Delta K_{-1} = 0$ ) were measured and analysed in ref. [1]. As a result, fairly accurate values of the rotational constants *B* and *C* were obtained but the



**Figure 1.** Molecular geometry of allyl isothiocyanate.

value of the  $A$  rotational constant remained relatively uncertain. Since allyl isothiocyanate is a relatively lighter open chain molecule the effect of centrifugal distortion on the rotational energy levels should be substantial. Although a partial CD analysis was done in [1], all the CD parameters could not be determined accurately because of the lack of sufficient data. However, this can be achieved by extending the microwave measurements to more higher rotational states and by incorporating  $b$ -type transitions ( $\Delta K_{-1} \neq 0$ ) in the least-squares analysis. The inclusion of  $b$ -type transitions facilitates an accurate determination of the  $A$  rotational constant as well.

In the present paper, we report a reanalysis of the microwave spectrum of allyl isothiocyanate in the ground vibrational state ( $v = 0$ ) by incorporating some more new  $b$ -type  $Q$ - and  $R$ -branch transitions and by extending the frequency range up to 37.0 GHz. The resultant least-squares fit of all the new and previously reported [1] microwave data gives more accurate values of all the rotational and CD constants.

## 2. Experimental details

The sample of allyl isothiocyanate was obtained from Aldrich Chemical Co. (quoted purity 97%) and was used without further purification. The microwave spectrum was observed at room temperature with a conventional 100 kHz Stark modulated microwave spectrometer. For frequency measurement in the range 32.0–37.0 GHz, an Okaya 35V10 klystron was used as a frequency source. The method of frequency measurement was described in [6]. Sample pressure was maintained at around 30 mTorr throughout the experiment. The Stark voltage was kept around 500 V/cm. The uncertainty in frequency measurement was estimated to be around  $\pm 0.2$  MHz.

## 3. Analysis of the spectrum

### 3.1 $a$ -Type spectrum

The  $C$ -gauche conformer of allyl isothiocyanate belongs to a near symmetric prolate rotor ( $\kappa \approx -0.96$ ) with strong  $a$ -type spectrum. In [1] 36  $a$ -type  $R$ -branch transitions were

measured with  $J_{\max} = 10$ . The resultant least-squares fit provided a set of rotational and some CD ( $\tau$  parameters) constants where  $\tau_{aaaa}$  remained undetermined. Using these constants,  $a$ -type spectrum was predicted up to 37 GHz which covers  $J = 14 \leftarrow 13$  and  $J = 15 \leftarrow 14$  series. 17 new transitions with different  $K_{-1}$  values were measured for these two series. The low  $K_{-1}$  lines were found within a few MHz of their predicted values. As  $K_{-1}$  increases further the shift from the predicted values increases due to centrifugal distortion effects and the entire  $K$  structure moved towards higher frequencies. All these new transitions were included in the least-squares fit along with the previously reported transition frequencies.

### 3.2 $b$ -Type spectrum

The analysis of the  $b$ -type spectrum starts with the assignment of  $b$ -type  $Q$ -branch lines. The results of dipole moment calculation from the model geometry in [1] give  $\mu_a = 2.90$  D and  $\mu_b = 1.78$  D. Hence the  $b$ -type lines are expected to be relatively weaker in intensity than those of  $a$ -type lines. First of all, three  $Q$ -branch transitions  $8(3,6) \leftarrow 8(2,7)$ ,  $9(3,7) \leftarrow 9(2,8)$  and  $10(3,8) \leftarrow 10(2,9)$  were assigned by a  $Q$ -branch plot, taking all probable lines within  $\pm 200$  MHz of the predicted frequency, keeping the intensity factor and the uncertainty of the  $A$  rotational constant in [1] in mind. Subsequently, other  $Q$ -branch lines were predicted, measured and included in the least-squares fit along with the  $a$ -type transitions. Although a reasonably good fit was obtained, the rotational constant  $A$  and the centrifugal distortion constant  $D_K$  could not be determined independently. The resultant correlation matrix of the fit indicated a strong correlation between  $A$  and  $D_K$  (matrix element between  $A$  and  $D_K = 1.000$ ). This was partly removed when the two  $K = 2 \leftarrow 1$  transitions of  $J = 6 \leftarrow 5$  were assigned and included in the fit. Now,  $A$  and  $D_K$  were allowed to vary as independent fitting parameters in the iterative least-squares analysis. Finally, 60  $a$ - and  $b$ -type transitions were used in the least-squares fit. Watson's  $s$ -reduction Hamiltonian [7] in the  $I^r$ -representation was used for the analysis of the spectrum. This Hamiltonian has been found to be more suitable [8] for the analysis of the rotational spectrum of near symmetric top molecules. The resultant fit gives reasonably accurate values for both  $A$  and  $D_K$  along with other centrifugal distortion parameters. The inclusion of two sextic distortion constants  $H_J$  and  $H_{JK}$  improved the quality of the fit. The measured old and new transitions, their assignments and the resultant rotational and centrifugal distortion constants obtained from the final cycle of the least-squares analysis are presented in tables 1 and 2 respectively. A separate least-squares fit using the same Hamiltonian [7] was done with the data of [1]. The CD constant  $D_K$  was fixed to zero because only  $a$ -type transitions are involved in this case. The resultant parameters are also shown in table 2 for comparison.

## 4. Discussion

The present reanalysis of the ground state microwave spectrum of allyl isothiocyanate provides a complete set of rotational and centrifugal distortion constants for the C-gauche conformer of this molecule. This was made possible by assigning new  $b$ -type  $Q$ - and  $R$ -branch transitions in the extended frequency region. The rotational constant  $A$  has been

**Table 1.** Observed rotational transition frequencies of the C-gauche conformer of allyl isothiocyanate in the ground vibrational state (in MHz).

$J'$	Transition					Observed frequency	Obs.-Calc.
	$K'_{-1}$	$K'_{+1}$	$J$	$K_{-1}$	$K_{+1}$		
6	0	6	5	0	5	14193.45 <sup>a</sup>	-0.01
6	1	5	5	1	4	14632.80 <sup>a</sup>	-0.22
6	2	5	5	2	4	14251.90 <sup>a</sup>	-0.24
6	2	4	5	2	3	14318.80 <sup>a</sup>	0.14
6	3	4	5	3	3	14274.68 <sup>a</sup>	-0.03
6	3	3	5	3	2	14275.61 <sup>a</sup>	-0.13
6	2	5	5	1	4	33558.40	-0.01
6	2	4	5	1	5	35635.25	0.01
7	0	7	6	0	6	16530.30 <sup>a</sup>	-0.47
7	1	7	6	1	6	16157.35 <sup>a</sup>	0.25
7	1	6	6	1	5	17063.65 <sup>a</sup>	-0.32
7	2	6	6	2	5	16621.50 <sup>a</sup>	-0.35
7	3	5	6	3	4	16656.53 <sup>a</sup>	0.27
7	3	4	6	3	3	16658.62 <sup>a</sup>	0.05
7	5	2	6	5	1	16661.80 <sup>a</sup>	-0.18
8	2	7	7	2	6	18989.00 <sup>a,b</sup>	0.08
8	2	6	7	2	5	19146.50 <sup>a,b</sup>	-0.19
8	3	6	7	3	5	19038.80 <sup>a,b</sup>	0.13
8	3	5	7	3	4	19043.00 <sup>a,b</sup>	-0.30
8	6	2	7	6	1	19051.20 <sup>a</sup>	-0.34
8	3	6	8	2	7	34004.22	0.37
8	3	5	8	2	6	33615.25	-0.13
9	0	9	8	0	8	21166.90 <sup>a</sup>	-0.28
9	1	9	8	1	8	20750.60 <sup>a</sup>	0.19
9	1	8	8	1	7	21913.50 <sup>a</sup>	0.27
9	2	8	8	2	7	21353.45 <sup>a,b</sup>	0.50
9	2	7	8	2	6	21576.50 <sup>a,b</sup>	0.55
9	3	7	8	3	6	21421.80 <sup>a,b</sup>	-0.09
9	3	6	8	3	5	21430.20 <sup>a,b</sup>	-0.17
9	5	4	8	5	3	21424.10 <sup>a</sup>	-0.27
9	6	3	8	6	2	21433.45 <sup>a</sup>	0.15
9	7	2	8	7	1	21445.90 <sup>a</sup>	0.28
9	3	7	9	2	8	34072.37	-0.41
9	3	6	9	2	7	33470.03	0.24
10	2	9	9	2	8	23714.00 <sup>a</sup>	0.45
10	3	8	9	3	7	23806.40 <sup>a,b</sup>	0.62
10	6	4	9	6	3	23815.35 <sup>a</sup>	0.23
10	7	3	9	7	2	23828.43 <sup>a</sup>	0.10
10	8	2	9	8	1	23845.00 <sup>a</sup>	0.18
10	9	1	9	9	0	23864.20 <sup>a</sup>	-0.01
10	3	8	10	2	9	34164.55	-0.46
11	1	11	10	1	10	25327.90 <sup>a</sup>	-0.38
14	1	13	13	1	12	33918.93	0.11
14	2	13	13	2	12	33113.55	0.28
14	2	12	13	2	11	33859.50	-0.40
14	3	11	13	3	10	33422.00	-0.18
14	4	10	13	4	9	33343.55	-0.27
14	5	10	13	5	9	33335.00	-0.51

contd...

**Table 1.** Contd...

$J'$	Transition					Observed Frequency	Obs.-Calc.
	$K'_{-1}$	$K'_{+1}$	$J$	$K_{-1}$	$K_{+1}$		
14	6	8	13	6	7	33342.35	-0.25
14	7	7	13	7	6	33357.70	0.02
14	8	6	13	8	5	33378.57	0.04
14	9	5	13	9	4	33403.60	-0.52
14	12	2	13	12	1	33504.85	-0.19
15	0	15	14	0	14	34762.25	0.18
15	4	12	14	4	11	35727.35	0.31
15	6	9	14	6	8	35723.95	-0.38
15	7	8	14	7	7	35739.70	0.34
15	8	7	14	8	6	35761.25	0.28
15	9	6	14	9	5	35788.30	0.43
15	3	13	15	2	14	35131.30	0.39

<sup>a</sup>Ref. [1].<sup>b</sup> RF-microwave double resonance assignment.**Table 2.** Ground state molecular constants of allyl isothiocyanate (C-gauche conformer).

	Present work	Using ref. [1] data
$A/\text{MHz}$	$7931.86 \pm 0.13$	$7918.25 \pm 5.50$
$B/\text{MHz}$	$1253.05 \pm 0.02$	$1252.94 \pm 0.03$
$C/\text{MHz}$	$1123.57 \pm 0.02$	$1123.66 \pm 0.03$
$D_J/\text{kHz}$	$1.48 \pm 0.13$	$1.48 \pm 0.06$
$D_{JK}/\text{kHz}$	$-60.69 \pm 0.29$	$-59.91 \pm 0.11$
$D_K/\text{kHz}$	$-2351.46 \pm 10.98$	$0.0^a$
$d_1/\text{kHz}$	$1.02 \pm 0.02$	$1.36 \pm 0.09$
$d_2/\text{kHz}$	$0.95 \pm 0.01$	$0.86 \pm 0.04$
$H_J/\text{Hz}$	$-1.23 \pm 0.32$	
$H_{JK}/\text{Hz}$	$-1.21 \pm 0.78$	

<sup>a</sup> Fixed.

determined with much higher precision. However, it must be mentioned here that, although the inclusion of two  $K = 2 \leftarrow 1$  transitions of  $J = 6 \leftarrow 5$  has partly removed the correlation between  $A$  and  $D_K$ , still there exists a fair amount of correlation between them (correlation matrix element between  $A$  and  $D_K = 0.9833$ ). As a result, the  $D_K$  constant could not be determined as accurately as other quartic distortion constants. But it gives a good estimate of its magnitude which is found to be the largest among all the CD parameters. Furthermore, the inclusion of two sextic CD constants  $H_J$  and  $H_{JK}$  in the least-squares analysis, which was felt necessary to improve the overall quality of the fit, gives small but finite values for these constants.

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