Centrifugal distortion effects in the microwave spectrum of allyl alcohol

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Abstract. The ground state rotational spectrum of allyl alcohol has been reinvestigated in the frequency range 12·5—40·0 GHz. A detailed centrifugal distortion analysis has been carried out and the J-value of the assigned transitions has been extended to 45. The evaluated parameters are presented.

1. Introduction

The microwave spectra of allyl alcohol in the ground and excited vibrational states have been investigated by Murty and Curl (1967) on the basis of a rigid rotor model. For the ground state spectrum, they have assigned twenty transitions involving angular momentum states upto $J = 6$. However, the effect of centrifugal distortion on the rotational spectrum becomes appreciable when higher angular momentum states are taken into account. Moreover, since allyl alcohol is a nearly prolate symmetric top molecule ($k \simeq -0.99$), the effect of centrifugal distortion on its rotational energy levels is of considerable interest. In this paper, we have made a centrifugal distortion analysis of this molecule incorporating a number of new transitions and thereby extending the J value to 45.

It has been pointed out by Van Eijck (1974) that the Watson's Hamiltonian (Watson 1967, 1968) widely used for the centrifugal distortion analysis is not suitable for this type of molecule. He has shown that Watson's choice for the arbitrary parameter S_{111} results in a poor convergence for the Hamiltonian of nearly symmetric top molecule. He proposed another choice for the same parameter which redefined the centrifugal distortion parameters in such a manner that they remain well-defined in the symmetric top limit. The form of the Hamiltonian (Van Eijck 1974; Typke 1976) is given below

$$H = H_0 - D'_J P^4 - D'_{JK} P^2 P_z^2 - D'_K P_z^4 - 2 \delta'_J P^2 (P_x^2 - P_y^2)$$

$$+ 2 R'_6 (\mathcal{O}) + H'_J P^6 + H'_{JK} P^4 P_z^2 + H'_{KJ} P^2 P_z^4 + H'_K P_z^6$$

$$+ H'_5 P^4 (P_x^2 - P_y^2) + \tfrac{1}{2} H'_6 P^2 \mathcal{O} + \dot{H}'_{10} (P_x^2 - P_y^2)^3$$

with $H_0 = X' P_x^2 + Y' P_y^2 + Z' P_z^2$ and $\mathcal{O} = P_x^4 + P_y^4 - 3 (P_x^2 P_y^2 + P_y^2 P_x^2)$,

where H_0 is the rigid rotor Hamiltonian. D_J', D_{JK}', etc. are quartic and H_J', H_{JK}', etc. are sextic centrifugal distortion constants. In view of the current interest in the centrifugal distortion analysis of nearly symmetric top molecules—mainly the applicability of the above Hamiltonian—we have undertaken such an analysis for allyl alcohol in the ground vibrational state using this Hamiltonian. In such an analysis, the judicious choice of representation has an important role in the goodness of fit of the observed spectrum. In the present analysis the III^r representation $(X' \longleftrightarrow a, Y' \longleftrightarrow b, Z' \longleftrightarrow c)$ has been used, whereas the I^r representation $(X' \longleftrightarrow b, Y' \longleftrightarrow c, Z' \longleftrightarrow a)$ resulted in a poor fit. The CD parameters were determined using the program written by Dr V Typke of ULM University.

2. Experimental details

The normal sample of allyl alcohol was obtained commercially and was used without further purification. The purity of the sample as stated by the manufacturer is 98%. The spectrum was observed at room temperature using a 100 kHz Stark modulated microwave spectrometer. The maximum experimental uncertainty in the measurement is estimated to be $\pm$ 0·2 MHz. The sample pressure was kept around 10^{-2} mm Hg during measurements. The Stark voltage was kept approximately at 300 V/cm.

3. Results and analysis of the spectrum

Allyl alcohol has a large μ_a component and a comparatively small μ_c component. Very small value of $|\mu_b|$ restrains the observation of any b-type transitions. From the rigid rotor analysis of Murty and Curl (1967), we have three rotational constants to start with. With these values a spectrum was generated. The low J lines appeared within a few megacycles of the predicted values. The newly observed low J transitions have been included with the previously reported lines and a least squares analysis has been carried out to evaluate the quartic centrifugal distortion constants. Gradually more and more higher J transitions were predicated, measured and included in the fit to refine the centrifugal distortion parameters. Unit weight has been assigned to all the transitions used in the analysis. However, all centrifugal distortion parameters were not well determined. In fact, the standard deviation of δ_J' has been found to be larger than its absolute magnitude. So δ_J' has been set to zero and the analysis was repeated to evaluate the three rotational and four quartic centrifugal distortion constants. Different transitions used in the analysis, the difference between the calculated and observed frequencies and the centrifugal distortion corrections are listed in table 1. The inclusion of some selective sextic parameters constraining others to zero did not improve the fit. Moreover, the sextic parameters came out statistically undetermined. The evaluated parameters are listed in table 2 together with their respective standard deviation and their correlation matrix. All the parameters are statistically well determined. Mention must be made that the

whole procedure for the analysis of the spectrum was also repeated using Watson's Hamiltonian. However, such an analysis does not lead to the convergence in the least squares iterative method which is consistent with the theoretical considerations.

Table 1. Transitions for the ground vibrational state of allyl alcohol (in MHz)

J'	K'_{-1}	K'_{+1}	J	K_{-1}	K_{+1}	Observed frequency	Cal.−Obs.	CD Correction
1	0	1	0	0	0	8551·60[b]	−0·049	0·073
2	0	2	1	0	1	17102·90[b]	−0·107	0·163
2	1	2	1	1	1	17007·90[b]	0·209	−0·069
2	1	1	1	0	1	38562·44[b]	−0·354	0·383
2	1	1	1	1	0	17198·50[b]	−0·290	0·360
2	2	0	3	1	2	38009·11[b]	0·416	−0·688
3	0	3	2	0	2	25653·00[b]	0·418	−0·310
3	1	3	2	1	2	25511·50[b]	0·474	−0·255
3	1	2	2	1	1	25797·40[b]	−0·247	0·389
3	2	2	2	2	1	25655·60[b]	−0·357	1·018
4	0	4	3	0	3	34202·60[b]	0·516	−0·329
4	1	3	3	1	2	34395·80[b]	0·102	0·157
4	3	2	3	3	1	34208·50[b]	−0·694	1·756
1	1	1	1	0	1	21268·70[b]	0·131	−0·131
2	1	2	2	0	2	21173·90[b]	0·246	−0·163
3	1	3	3	0	3	21032·20[b]	0·503	−0·309
4	1	4	4	0	4	20844·90[b]	0·298	0·016
5	1	5	5	0	5	20612·30[b]	0·265	0·154
6	1	6	6	0	6	20335·50[b]	0·465	0·007
9	3	7	10	2	9	21074·45	−0·633	−29·799
12	1	12	11	2	10	34865·12	−0·408	−54·255
12	4	9	13	3	11	38011·70	0·479	−1·347
14	2	12	13	3	10	13447·05	0·424	−116·704
14	4	10	15	3	12	20894·43	−0·680	16·466
15	1	15	15	0	15	16170·30	0·438	−13·753
15	2	13	14	3	11	22092·85	−0·491	−149·119
16	1	16	16	0	16	15566·95	−0·173	−18·328
20	3	18	19	4	16	21992·00	−0·127	42·639
21	1	20	21	1	21	22106·00	0·113	230·297
24	4	21	23	5	19	13523·25	−0·513	−15·965
32	5	27	31	6	25	39371·56	0·016	−43·279
33	8	25	34	7	27	28933·48	−0·498	68·455
37	2	35	37	2	36	13008·59	0·755	−8392·083
39	2	38	39	1	38	34616·56	0·133	3252·842
39	7	32	38	8	30	13886·75	0·394	−89·995
40	2	38	40	2	39	16904·20	−0·919	−10744·001
40	7	33	39	8	31	22456·10	−0·216	−93·038
43	2	41	43	2	42	21419·00	0·018	−13359·778
44	8	36	43	9	34	13997·57	−0·260	−126·220
45	2	43	45	2	44	24790·65	0·250	−15214·597

[b]Frequencies taken from Murty and Curl (1967).

Table 2. Ground state molecular constants of allyl alcohol and correlation matrix.[a]

A'/MHz	25592·1371(854)	1·000						
B'/MHz	4323·3065(146)	0·946	1·000					
C'/MHz	4228·2209(143)	0·944	0·991	1·000				
D'_J/kHz	4·4239(491)	0·412	0·394	0·410	1·000			
D'_{JK}/kHz	−42·3089(740)	−0·421	−0·391	−0·406	−0·998	1·000		
D'_K/kHz	43·4043(355)	0·429	0·398	0·414	0·987	−0·995	1·000	
δ'_J/kHz	0·0[c]							
R'_6/kHz	−0·1074(191)	0·413	0·382	0·399	0·999	−0·998	0·988	1·000

[a]The uncertainties shown in parantheses are in units of last digit and are standard errors.
[c]Constrained value.

4. Conclusion

The reduced Hamiltonian proposed by Van Eijck and Typke appears to be more suitable for the centrifugal distortion analysis of a nearly symmetric top molecule where the conventional Watson's Hamiltonian fails miserably.

Acknowledgements

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