Centrifugal Distortion Effect in the Microwave Spectrum of 1,3-Dioxane-5-ol

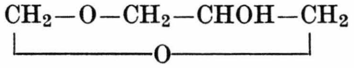
A. Roman, J. L. Alonso *, and F. Mata
Departamento de Química-Física, Facultad de Ciencias, Universidad de Valladolid, Spain

Z. Naturforsch. **36a**, 622–625 (1981); received April 4, 1981

The microwave spectrum of 1,3-Dioxane-5-ol has been analysed in the frequency region 18.0–40.0 GHz and up to $J = 30$. The analysis gives refined rotational constants and values for the quartic centrifugal distortion parameters. Comparison is made between the results using two forms of the quartic Hamiltonian.

Introduction

The first microwave study of 1,3-Dioxane-5-ol


$$\mathrm{CH_2{-}O{-}CH_2{-}CHOH{-}CH_2}\ \text{(ring closed by O)}$$

was made by Alonso and Wilson [1] who analysed the 1,3-Dioxane-5-ol transitions up to $J = 12$. The molecule has been found to exit in a chair form conformation. Only one axial conformer was detected with an intramolecular hydrogen bond of the O–H ... O type. The effects of nonrigidity were noticed but not included in the earlier analysis. The present paper gives the results of an investigation of the centrifugal perturbation of 1,3-Dioxane-5-ol within the framework of the Watson theory [2], using a large number of frequencies for microwave transitions (140 for the ground state) and large values of the quantum number J (up to $J = 30$). In this way, we hoped to extend our understanding of the centrifugal distortion effects in the heterocyclic molecules.

Experimental

The sample of 1,3-Dioxan-5-ol was prepared according to the method of Hibbert and Carter [3]. Microwave spectra were taken with a Hewlett-Packard Model 8460 A MRR spectrometer with a Stark cell modulation frequency of 33.3 KHz. All frequencies were measured at room temperature and the accuracy was estimated to be better than ± 0.05 MHz.

Analysis of the Spectrum

The molecule 1,3-Dioxane-5-ol is an asymmetric top with *a*- and *c*-type spectrum. The reported spectrum of the molecule (1) mainly consists of low J, *a*- and *c*-type, R-branch transitions and a strong set of the Q-branch series of *c*-type. Assignement of the higher J transitions was greatly facilitated using preliminary poorly determined CD constants obtained from low J transitions. Using the augmented set of observed frequencies in the least-squares fit yielded new rotational constants and a first estimate of the CD coefficients. These new constants were used to predict the positions of till higher J transitions.

The data were analyzed using two computer programs. One was developed by Thomas [4] and the other by Kirchhoff [5]. The Thomas program, DISTO, uses the form of Watson's reduced Hamiltonian [2]

$$\begin{aligned} H = {} & \tilde{A}\,P_z^2 + \tilde{B}\,P_x^2 + \tilde{C}\,P_y^2 - \Delta_J P^4 \qquad (1)\\ & - \Delta_{JK} P^2 P_z^2 - \Delta_K P_z^4 - 2\,\delta_J P^2 (P_x^2 - P_y^2)\\ & - \delta_K [P_z^2 (P_x^2 - P_y^2) + (P_x^2 - P_y^2) P_z^2]\,, \end{aligned}$$

where $\tilde{A}$, $\tilde{B}$ and $\tilde{C}$ are the effective rotational constants and where Δ_J, Δ_{JK}, Δ_K, δ_J and δ_K are the quartic distortion coefficients. These are related to the Kivelson-Wilson constants [6]. Initially a rigid rotor spectrum is calculated from low J transitions, then the differences between the observed and calculated frequencies are fitted to the quartic centrifugal distortion constants. Using these distortion constants a semi-rigid rotor calculation is made, and then a new least-squares fitting is made to determine changes in the distortion constants which will improve the fit. This semi-rigid calcula-

---

Reprint requests to Dr. J. L. Alonso, Universidad de Valladolid, Facultad de Ciencias, Departamento de Quimica Fisica, Valladolid, Spanien.

0340-4811 / 81 / 0600-0622 $ 01.00/0. — Please order a reprint rather than making your own copy.

Dieses Werk wurde im Jahr 2013 vom Verlag Zeitschrift für Naturforschung in Zusammenarbeit mit der Max-Planck-Gesellschaft zur Förderung der Wissenschaften e.V. digitalisiert und unter folgender Lizenz veröffentlicht: Creative Commons Namensnennung-Keine Bearbeitung 3.0 Deutschland Lizenz.

Zum 01.01.2015 ist eine Anpassung der Lizenzbedingungen (Entfall der Creative Commons Lizenzbedingung „Keine Bearbeitung“) beabsichtigt, um eine Nachnutzung auch im Rahmen zukünftiger wissenschaftlicher Nutzungsformen zu ermöglichen.

This work has been digitalized and published in 2013 by Verlag Zeitschrift für Naturforschung in cooperation with the Max Planck Society for the Advancement of Science under a Creative Commons Attribution-NoDerivs 3.0 Germany License.

On 01.01.2015 it is planned to change the License Conditions (the removal of the Creative Commons License condition “no derivative works”). This is to allow reuse in the area of future scientific usage.

Table 1. Rotational and centrifugal distortion constants of 1,3-Dioxane-5-ol (in MHz) obtained from DISTO program.

Parameter[a]	GS	$v_a = 1$	$v_b = 1$
$\tilde{A}$	3913.5525 ± 0.0022	3916.577 ± 0.012	3918.2612 ± 0.0093
$\tilde{B}$	2922.7841 ± 0.0022	2920.343 ± 0.012	2914.8667 ± 0.0093
$\tilde{C}$	2193.4469 ± 0.0030	2194.674 ± 0.012	2184.5284 ± 0.0098
Δ_J	$(0.637 \pm 0.018) \times 10^{-3}$	$(3.19 \pm 0.28) \times 10^{-3}$	$(2.26 \pm 0.26) \times 10^{-3}$
Δ_{JK}	$-(0.958 \pm 0.041) \times 10^{-3}$	$-(0.85 \pm 0.11) \times 10^{-3}$	$-(0.82 \pm 0.10) \times 10^{-3}$
Δ_K	$(1.128 \pm 0.021) \times 10^{-3}$	$(1.07 \pm 0.10) \times 10^{-3}$	$(1.03 \pm 0.10) \times 10^{-3}$
δ_J	$(0.97 \pm 0.09) \times 10^{-4}$	$(0.11 \pm 0.06) \times 10^{-3}$	$(0.10 \pm 0.04) \times 10^{-3}$
δ_K	$(0.16 \pm 0.06) \times 10^{-3}$	—[d]	—[d]
N[b]	140	89	88
S[c]	0.048	0.48	0.38

[a] Uncertainty is the standard deviation. [b] Number of lines fitted. [c] Standard deviation of the calculation.
[d] Not determined from the data.

tion may be repeated till the rms deviation do not decrease. The constants for the ground state and excited vibrational states obtained as a result of the analysis are given in Table 1. The microwave spectrum data were inadequate for determining the constant δ_K for the excited states. Copies of the calculated spectrum may be obtained from the authors on request.

The same sets of transitions next were analyzed using the Kirchhoff program [5], CDANAL, which employs the form of Watson's reduced Hamiltonian

$$\begin{aligned} H &= H_2 + H_4 + H_6\,, \\ H_2 &= A''\,P_a^2 + B''\,P_b^2 + C''\,P_c^2\,, \\ H_4 &= 1/4 \sum_{\alpha=a,b,c} \tau''_{\alpha\alpha\alpha\alpha}\,P_\alpha^4 + \tau_1 P_1^4 + \tau_2 P_2^4 \\ &\quad + \tau_3 P_3^4\,, \end{aligned} \tag{2}$$

where A'', B'' and C'' are the effective rotational constants and $\tau''_{\alpha\alpha\alpha\alpha}$, τ_1 and τ_2 are the quartic distortion constants. For the calculations presented in this paper, only terms up H_4 will be considered. The rotational energy states are obtained by diagonalizing the quartic Hamiltonian $H_2 + H_4$. These rotational energies are nonlinear functions of the quadratic and quartic parameters and were approximately linearized by a perturbation theory treatment because the rotational Hamiltonian may be written as a linear function of the rotational parameters with angular momentum operators (5) expressed in the general form

$$H = \sum_\alpha C_\alpha X_\alpha\,, \tag{3}$$

where X are hermitian operators and C are the corresponding parameter. The energies are given by

$$W_i = \sum_\alpha C_\alpha \langle X_\alpha \rangle_i\,. \tag{4}$$

An iterative calculation and a linear least-squares fit were performed in order to calculate corrections to C_α parameters (rotational and quartic centrifugal distortion constants simultaneously). After n iterations H may be represented by

$$\begin{aligned} H &= H^{(n)} + \Delta^{(n)} \quad \text{where} \\ H^{(n)} &= \sum_\alpha C_\alpha^{(n)} X_\alpha \quad \text{and} \\ \Delta^{(n)} &= \sum \delta_\alpha^{(n)} X_\alpha\,. \end{aligned} \tag{5}$$

$\Delta^{(n)}$ represents a perturbation term and $\delta_\alpha^{(n)}$ represents the correction to the parameter $C_\alpha^{(n)}$. There corrections can be obtained by a least-squares fit of

$$\sum_\alpha \delta_\alpha^{(n)} \langle X_\alpha \rangle_i^{(n)} = W_i - \sum_\alpha C_\alpha^{(n)} \langle X_\alpha \rangle_i^{(n)}\,, \tag{6}$$

where W_i are the measured energies. The iterative procedure was assumed to have converged when the difference between the residuals from the least-squares fit of the spectrum and the residuals obtained after $H_2 + H_4$ was diagonalized with the new constants vanished for all the spectral observations. In this situation the corrections $\delta_\alpha^{(n)}$ were considered to be negligibly small.

The relation between the Watson form of $H_2 + H_4$ [3] and the Kivelson-Wilson form of $H_2 + H_4$ [7] has been described in detail by Kirchhoff (5) (see Table 2). The τ_3 coefficient has been added by Kirchhoff to transform the Kivelson-Wilson form to the Watson form and it is held constant during the fit. τ_3 is not a determinable coefficient, but is evaluated once the remaining eight parameters have been determined. The derived rotational and centrifugal distortion constants are presented in Table 2. It should be noted that the number of significant figures quoted for each parameter is greater than required by the standard deviation of that parameter. This precision is absolutely necessary to reproduce all the calculated frequencies within their standard deviations.

Table 2. Rotational and centrifugal distortion constants of 1,3-Dioxane-5-ol (in MHz) obtained from CDANAL program.

Watson's Parameters	GS	$v_a = 1$	$v_b = 1$
A''	3913.55344 ± 0.0023	3916.5832 ± 0.012	3918.2647 ± 0.0093
B''	2922.78455 ± 0.0022	2920.3476 ± 0.012	2914.8733 ± 0.0094
C''	2193.4474 ± 0.0030	2194.6824 ± 0.013	2184.5146 ± 0.012
τ_1	$(-3.8083 \pm 0.38) \times 10^{-3}$	$(-3.4813 \pm 0.33) \times 10^{-2}$	$(-2.3371 \pm 0.25) \times 10^{-2}$
τ_2	$(-1.3764 \pm 0.13) \times 10^{-3}$	$(-1.1719 \pm 0.11) \times 10^{-2}$	$(-7.8994 \pm 0.83) \times 10^{-3}$
τ_3	$(4.9 \pm 0.2) \times 10^{-2}$	0.22 ± 0.02	0.15 ± 0.01
τ''_{aaaa}	$(-3.2258 \pm 0.12) \times 10^{-3}$	$(-1.3623 \pm 0.11) \times 10^{-2}$	$(-9.7787 \pm 0.82) \times 10^{-3}$
τ''_{bbbb}	$(-3.3286 \pm 0.12) \times 10^{-3}$	$(-1.3639 \pm 0.11) \times 10^{-2}$	$(-9.7520 \pm 0.83) \times 10^{-3}$
τ''_{cccc}	$(-1.769 \pm 0.13) \times 10^{-3}$	$(-1.209 \pm 0.11) \times 10^{-2}$	$(-8.037 \pm 0.83) \times 10^{-3}$
N[b]	140	89	88
S[c]	0.050	0.075	0.073

Kivelson-Wilson Parameters	GS	$v_a = 1$	$v_b = 1$
A'	3913.5522 ± 0.0022	3916.577 ± 0.012	3918.2602 ± 0.0089
B'	2922.7848 ± 0.0022	2920.343 ± 0.012	2914.8701 ± 0.0090
C'	2193.4465 ± 0.0029	2194.676 ± 0.013	2184.511 ± 0.011
τ'_{bbcc}	$(-2.55 \pm 0.12) \times 10^{-3}$	$(-1.29 \pm 0.11) \times 10^{-2}$	$(-8.89 \pm 0.83) \times 10^{-3}$
τ'_{ccaa}	$(0.42 \pm 0.17) \times 10^{-3}$	$(-1.01 \pm 0.11) \times 10^{-2}$	$(-6.51 \pm 0.87) \times 10^{-3}$
τ'_{aabb}	$(-1.68 \pm 0.13) \times 10^{-3}$	$(-1.19 \pm 0.11) \times 10^{-2}$	$(-7.96 \pm 0.83) \times 10^{-3}$

$$A'' = A' - 1/2\,\tau'_{bbcc} \qquad \tau''_{\alpha\alpha\alpha\alpha} = \tau'_{\alpha\alpha\alpha\alpha} \quad \alpha = a, b, c$$

$$B'' = B' - 1/2\,\tau'_{aacc} \qquad \tau_1 = \tau'_{aabb} + \tau'_{bbcc} + \tau'_{ccaa}$$

$$C'' = C' - 1/2\,\tau'_{aabb}$$

$$\tau_2 = (A'/S)\,\tau'_{bbcc} + (P'/S)\,\tau'_{aacc} + (C'/S)\,\tau'_{aabb},$$

$$\text{where} \quad S = A' + B' + C'$$

[a] Uncertainty is the standard deviation. The number of significant figures quoted are necessary to reproduce all the calculated frequencies within their standard deviation.

[b] Number of lines fitted. [c] Standard deviation of the calculation $S = \left[\frac{\sum_{i=1}^{i=N} (\nu_{i\,\text{obs.}} - \nu_{i\,\text{calc.}})^2}{N-8} \right]^{1/2}$.

Table 3. Correlation Matrix for the ground state.

$\tilde{A}$	1.000							
$\tilde{B}$	−0.405	1.000						
$\tilde{C}$	0.665	−0.433	1.000					
Δ_J	0.273	−0.941	0.357	1.000				
Δ_{JK}	0.324	−0.946	0.375	0.997	1.000			
Δ_K	0.338	−0.949	0.387	0.997	0.999	1.000		
δ_J	−0.207	0.025	−0.170	0.056	0.074	0.039	1.000	
δ_K	0.048	0.076	−0.065	−0.139	−0.159	−0.132	−0.954	1.000

A''	1.000								
B''	0.943	1.000							
C''	0.835	0.770	1.000						
τ_1	−0.907	−0.883	−0.895	1.000					
τ_2	−0.906	−0.881	−0.895	0.999	1.000				
τ_2	0.758	0.767	0.765	−0.783	−0.775	1.000			
τ''_{aaaa}	−0.924	−0.891	−0.887	0.996	0.996	−0.812	1.000		
τ''_{bbbb}	−0.913	−0.898	−0.888	0.997	0.996	−0.819	0.998	1.000	
τ''_{cccc}	−0.854	−0.843	−0.876	0.914	0.909	−0.965	0.935	0.934	1.000

Discussion

A complete calculation including centrifugal distortion effects has been made for the rotational energy levels of 1,3-Dioxan-5-ol up to $J = 30$ in the ground and two vibrational states. The results indicate that the ability to obtain well-determined quartic coefficients can depend on the form of the quartic Hamiltonian. Thus, the percent uncertainties in the τ coefficients from CDANAL fit (~ 10 percent) are larger than those in the Δ coefficients in the DISTO fit (~ 5 percent). It is evident that much larger centrifugal distortion frequency shifts than those observed in the present study are required to bring the uncertainty limits of the τ's with those of Δ's. Also, there was found to be much less correlation among the quartic coefficients in the DISTO analysis than the coefficients in the CDANAL analysis (see Table 3). In the DISTO analysis there are four correlation coefficients between the Δ's parameters greater than 0.9: $(\Delta_{JK}, \Delta_J) = 0.997$, $(\Delta_K, \Delta_{JK}) = 0.999$, $(\Delta_J, \Delta_K) = 0.997$ and $(\delta_J, \delta_K) = 0.954$. The higher correlation between the τ's coefficients in the CDANAL analysis provides a confirmation that the linear combinations of the Δ's are better determined than the τ coefficients. A similar behaviour has been found in the centrifugal distortion analysis of 1,3-Dioxane, Tetrahydropyran and Piperidine [8].

One point is interesting concerning to the consistency of the results obtained. By using the expressions (6) to convert the observed τ's of Table 2 to the Δ's of Table 1, we are able to reproduce very well the Δ's.

[1] J. L. Alonso and E. B. Wilson, Jr., J. Amer. Chem. Soc. **102,** 1248 (1980).

[2] J. K. G. Watson, J. Chem. Phys. **46,** 1935 (1967) and J. Chem. Phys. **48,** 4517 (1968).

[3] H. Hibbert and N. M. Carter; J. Amer. Chem. Soc. **50,** 3120 (1928).

[4] C. Thomas, Harvard University.

[5] W. H. Kirchhoff, J. Mol. Spectrosc. **41,** 333 (1972).

[6] W. Gordy and R. L. Cook, Microwave Molecular Spectra, W. West, Ed: Chapter 8; John Wiley-Intersci., New York 1970.

[7] D. Kivelson and E. B. Wilson, Jr., J. Chem. Phys. **20,** 1575 (1952) and J. Chem. Phys. **21,** 1229 (1953).

[8] R. S. Lowe and R. Kewley, J. Mol. Spectrosc. **60,** 312 (1976).