

Centrifugal Distortion in Thietane

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The microwave spectrum of thietane (trimethylene sulfide) has been remeasured for the $v=0, 1$ states of the puckering vibration in the region 8 to 40 GHz. New high- J Q-branch transitions have been assigned.

The spectrum has been interpreted using an effective two-level vibration-rotation Hamiltonian including quartic and sextic centrifugal distortion constants.

In the last decade there has been considerable interest in the microwave spectra of small ring compounds with a low-frequency out-of-plane vibration.¹⁻⁷ These investigations have mainly been concerned with determining the anharmonic potential for this vibration from the vibrational dependence of the rotational constants. Little attention has, however, been paid to the centrifugal distortion and the additional information that can be extracted from the corresponding constants.

Recently, Creswell and Mills⁸ have investigated the spectra of oxetane and deuterated species using an effective Hamiltonian for each of the puckering vibrational states. The distortion constants found show the same zig-zag dependence of the puckering quantum number as the rotational constants. This could be explained in terms of the double minimum potential for this vibration.

In thietane the separation between the $v=0, 1$ levels of the puckering vibration is approximately 8230 MHz¹ and nearly equal rotational and distortion constants are expected for these states.

The present work was also motivated by recent results on cyanamide- d_3 , where centrifugal distortion is essential for describing the observed spectrum.⁸

EXPERIMENTAL

The sample of thietane was a commercial product from Fluka AG, which was further purified by vacuum distillation. The spectrum was recorded on a Hewlett-Packard 8460A MRR spectrometer in Copenhagen. Sample temperatures varied from -40 to 25°C at pressures less than 10μ . Frequencies were measured to ± 0.05 MHz.

EFFECTIVE HAMILTONIAN

Angular momentum, arising from the large-amplitude puckering motion, enters into the Hamiltonian, to a first order approximation, in two terms,⁹ $L_b J_b$ and $\mu_{ac}(J_a J_c + J_c J_a)$. L_b contains the b component of internal angular momentum. The ambiguity of these vibration-rotation interactions was first noticed by Harris *et al.*¹ who pointed out that the two terms are physically equivalent. Further, the angular momentum from the vibration can be distributed in any ratio between L_b and μ_{ac} depending only on the axis system chosen for developing the Hamiltonian. This relationship was later formulated by Pickett.¹⁰

Thus, it is not possible at the same time to define a molecule-fixed rotating axis system and determine both interaction constants. It is necessary to fix either L_b or μ_{ac} and the most reasonable choice is the limit, $\mu_{ac}=0$ or $L_b=0$. The first choice corresponds to the principal axis system (PAS), the second, denoted as the reduced axis system (RAS),¹⁰ is close to the better-known Eckart system. Transformation between the two limiting systems is merely equivalent to a dynamic rotation about the b -axis,

$$H_{\text{RAS}} = \exp[i\theta(Q)J_b] H_{\text{PAS}} \exp[-i\theta(Q)J_b]$$

Q being the large-amplitude coordinate and $\theta(Q)$ some well-defined operator.

In thietane the $v=0, 1$ states of the puckering vibration are well separated from the rest of the vibrational energy levels in the molecule. By projecting the total vibration-rotation Hamiltonian into the subspace consisting of this doublet it is possible to produce an effective two-level rotational Hamiltonian. Further reduction of the Hamiltonian to a form containing only five quartic and seven sextic distortion constants for each state is necessary before fitting the data.

In this work, the observed spectrum was fitted to the following reduced Hamiltonian

$$H_{\text{red}} = |0\rangle\langle 0| (H_r^{(0)} + H_d^{(0)}) |0\rangle\langle 0| + |1\rangle\langle 1| (H_r^{(1)} + H_d^{(1)}) \\ + W_{01} |1\rangle\langle 0| + |0\rangle\langle 1| + |1\rangle\langle 1| H_c |0\rangle\langle 0|$$

$$H_r^{(v)} = X^{(v)} J_x^2 + Y^{(v)} J_y^2 + Z^{(v)} J_z^2$$

$$H_d^{(v)} = \{\text{Watson quartic and sextic distortion}\}^{(v)}$$

$$W_{01} = \langle 1|H_{\text{vib}}^0|0\rangle - \langle 0|H_{\text{vib}}^0|1\rangle$$

$$H_c = \mu_{yz}(J_y J_z + J_x J_y) \text{ or } L_x J_x$$

RESULTS

In order to establish the most suitable coordinate system for developing the Hamiltonian all reported data on similar molecules were used. There was, however, no reliable evidence in favour of either system.

On the basis of the more accurate measurements on thietane, it soon became evident that the RAS system was superior to the PAS system. It was found that the Hamiltonian converged more rapidly if developed in the RAS system. Even in calculations based on transitions with J less than 6, where centrifugal distortion normally can be ignored, there was a marked difference in the goodness of the fit. Hence the RAS system was used in the later calculations.

The final assignment was then based on prediction, on Stark effect and on frequency fitting. A total of 169 transitions with J up to 50 was measured. It was found necessary to consider sextic centrifugal distortion in order to get a reasonable fit. Only one sextic constant could be determined for each state with significance. The least correlation between parameters was found using h_{JK} .

The derived parameters are given in Table 1. A list of frequencies and the correlation matrix is available from the author upon request.

Simultaneously with this work Wieser and Mills of the University of Reading have inves-

Table 1. Derived parameter (RAS) for the $v=0, 1$ states of the puckering vibration in thietane. Rotational constants (A, B, C), energy difference (W_{01}), coupling constant (μ_{yz}) and standard deviation (σ) in MHz. Quartic distortion constants ($\Delta J, \Delta_{JK}, \Delta_K, \delta J, \delta_K$) in kHz. Sextic distortion constant (h_{JK}) in Hz. Numbers in parentheses represent one standard deviation.

| | $v=0$ | $v=1$ |
|---|-----------------|-----------------|
| A | 10107.2018 (16) | 10107.5431 (13) |
| B | 6670.1426 (11) | 6670.0768 (11) |
| C | 4443.6175 (11) | 4444.2911 (11) |
| ΔJ | 2.386 (19) | 2.388 (20) |
| Δ_{JK} | -2.171 (60) | -2.113 (49) |
| Δ_K | 6.69 (10) | 6.769 (90) |
| δJ | 0.6119 (44) | 0.599 (30) |
| δ_K | 2.085 (33) | 1.954 (31) |
| h_{JK} | 0.0943 (37) | 0.0757 (19) |
| $W_{01} = 8231.961 (15) \quad \mu_{yz} = 121.3323 (40)$ | | |
| $\sigma = 0.019$ | | |

tigated the MW spectra of thietane and several deuterated species including the higher excited states of the puckering vibration. A detailed analysis of the vibrational dependence of the centrifugal distortion constants will be given by these authors.

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