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# New Measurements on the Frequency Doubling in the First Excited S–S Stretching State of HSSH

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More than 300 rotational transitions in the first excited S–S stretching state ($v_s = 1$) of the internal rotor disulfane (HSSH), occurring at frequencies up to 420 GHz, have been measured, most for the first time. The frequency doubling due to torsion in the $^rQ_0$ branch of transitions has been studied through $J = 75$ and has been found to have a small dependence on the rotational quantum number, which was not apparent in older data. In a previous paper it was shown that the size of the frequency doubling in the $v_s = 1$ state could be explained by a Fermi-type coupling with the manifold of torsionally excited states. Here we show that this mechanism is also capable of explaining the rotational dependence of the frequency doubling. 

## I. INTRODUCTION

The rotational and torsional–rotational spectra of the nearly perfect accidentally prolate symmetric top disulfane (HSSH) have proved to be of considerable interest and have led to an understanding of the potential for torsional motion (*1, 2*). The *c*-type rotational spectra for a variety of vibrational states show a frequency doubling, which is very small in the ground state (0.150 MHz) but is more pronounced in states that are torsionally excited and are characterized by torsional quantum number $v_t > 0$. The frequency doubling derives from the sum of two nearly identical splittings in torsional energy sublevels, which we have discussed previously (*1, 2*). These energy splittings are labelled $\Delta$ ($\tau$ = 4–1) and $\Delta$ ($\tau$ = 3–2), where the quantum number $\tau$ characterizes the four torsional sublevels associated with each value of $v_t$ in ascending order, only two of which ($\tau$ = 1, 4) exist for even values of the prolate quantum number $K$ and two of which ($\tau$ = 2, 3) exist for odd values of this quantum number (*1, 2*). The torsional selection rules are $\tau = 3 \leftrightarrow 1$ and $2 \leftrightarrow 4$ (*1*).

Recently, we undertook a theoretical investigation to explain the large size of the frequency doubling seen in the rotational spectrum of the first excited S–S stretching state ($v_s = 1$) (*3*). We showed that the frequency doubling can derive from a potential (Fermi-type) coupling between the $v_s = 1$ state and the manifold of torsionally excited states ($v_t > 0$) in which the torsional sublevel energy splitting is much larger than in



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$v_s = 1$ (*3*). Specifically, we demonstrated that to second order, $\Delta\nu$, the frequency doubling in the $v_s = 1$ state, is given approximately by the equation

$$\Delta\nu \approx \Delta\nu^{(0)} + \sum_{v_t} \frac{\{\Delta\nu_{v_t}^{(0)} - \Delta\nu^{(0)}\}|\langle v_t|\mathscr{H}'|v_s = 1\rangle|^2}{[E^{(0)}(v_s = 1) - E^{(0)}(v_t)]^2}, \quad (1)$$

where the superscript (0) indicates zeroth order, $\Delta\nu_{v_t}$ is the frequency doubling in the rotational spectrum of the torsional state characterized by $v_t$, $E^{(0)}$ is the zeroth-order energy of a vibrational state, $\mathscr{H}'$ is the perturbation operator that couples the $v_s = 1$ state and the torsional states (see Eq. (2) in Ref. (*3*)), and the sum is over all excited torsional states ($v_t \geqslant 1$). Equation (1) pertains if the perturbation matrix elements and energy denominators for the separate expressions for $\Delta(4\text{–}1)$ and $\Delta(3\text{–}2)$ are approximately the same (*3*). Since the $v_s = 1$ state involves no torsional excitation in zeroth order, $\Delta\nu^{(0)}$ is equal to the small observed frequency doubling in the ground state (0.150 MHz).

The matrix elements of $\mathscr{H}'$ have been calculated with the aid of quantum chemical techniques (*3*). It was found that the coupling element was by far strongest for the $v_t = 2$ state, lying 808 $cm^{-1}$ above the ground vibrational state and $\approx$300 $cm^{-1}$ above the $v_s = 1$ state. With the use of calculated matrix elements of $\mathscr{H}'$ and experimental values for the other parameters, Eq. (1) was utilized to calculate a value for $\Delta\nu$ of 2.2 MHz, which is approximately double the measured value of $\approx$1.00 MHz, obtained over 20 years ago (*4*). Although the calculated value for the frequency doubling is not in quantitative agreement with the measured value, the uncertainties in the theoretical procedure are large and it was felt that the plausibility of the coupling mechanism was demonstrated by the calculation (*3*).

The experimental data used for comparison with the theoretical work were taken before more modern techniques in millimeter-wave spectroscopy had been developed and it was thought that a reinvestigation of the millimeter-wave spectrum of the $v_s = 1$ state of HSSH would be profitable. In this paper, we report the results of this reinvestigation, in which, in addition to new measurements of assorted $P$ and $R$ branches as well as the ${}^rQ_1$ branch, the previously studied ${}^rQ_0$ branch of transitions at 138–140 GHz has been measured up to a much higher $J$ of 75. In the new investigation, a small, mainly quadratic dependence of the frequency doubling on $J$ in the ${}^rQ_0$ transitions has become apparent and we have attempted to ascertain whether this dependence is consistent with the perturbation mechanism of Eq. (1). As discussed below, it appears that our perturbation relation is indeed capable of explaining this weak $J$ dependence.

The remainder of this paper is organized as follows. In Section II, we discuss our experimental techniques and the spectral assignment and analysis, whereas in Section III, we first modify Eq. (1) to include rotational effects and then compare the deduced rotational dependence of $\Delta\nu$ for the ${}^rQ_0$-branch transitions with that measured in the laboratory.

## II. EXPERIMENTAL DETAILS

The ${}^rQ_0$-branch rotational transitions of HSSH in its first excited S–S stretching state ($v_s = 1$) were recorded and assigned through $J = 43$ at the time when the rotational spectrum of disulfane was first studied (*4*). However, the greater sensitivity of a present-day digitized millimeter-wave spectrometer permits a more facile recording of the $v_s = 1$ state *P*- and *R*-branch transitions needed for a full rotational analysis. The digitized spectrometer used in this work has been discussed previously (*5, 6*). Table I contains our newly measured data which consist of $^rQ_0$- and $^rQ_1$-branch transitions, as well as transitions from the $^rP_0$, $^rR_0$, $^rP_1$, and $^rP_2$ branches. All transitions are *c*-type (*1*). An overview of the newly measured transitions as well as the $^rQ_0$-branch lines is given in the Fortrat diagram in Fig. 1. The measurement accuracy is estimated to be 10 kHz for unblended lines. A small but relatively uncongested region of the $^rQ_1$ branch near 420 GHz is shown in Fig. 2. Comparison of this digitally obtained spectrum with the analogous grand-state spectrum obtained with a lock-in amplifier 20 years ago (see Fig. 1 of Ref. (*7*)) serves as a good test of present day sensitivity. In addition, the rotational spectral lines of the $v_s = 1$ state show the 3:1 intensity alteration seen previously. The samples of HSSH were kindly provided by Dr. Hahn from the Institute for Inorganic Chemistry at the University of Cologne.

The 1 MHz frequency doubling caused by torsional motion is apparent in all of the $v_s = 1$ data (see Fig. 2). However, only in the large *J* range of the $^rQ_0$-branch series of transitions is there any evidence for a small rotational dependence to the doubling. The rotational dependence of the frequency doubling in the $^rQ_0$ branch is shown in Fig. 3, where it can be seen to have mainly a quadratic dependence on *J*, which, from theoretical considerations (see Section III), we take to be a $J(J+1)$ dependence.

The data in Table I were analyzed by the following procedure. The torsional doubling the $^rQ_0$-branch series of lines was fit to a power series expression in $J(J+1)$,

$$\Delta\nu(J) = 0.8798 \text{ MHz} + 0.0408 \text{ kHz } J(J+1) + 0.00204 \text{ Hz } [J(J+1)]^2 \quad (2a)$$

$$= 0.8798 \text{ MHz } \{1 + (4.64 \times 10^{-5})J(J+1) + (2.32 \times 10^{-9})[J(J+1)]^2\}, \quad (2b)$$

and the term independent of *J*, 0.8798 MHz, divided by two to obtain the rotationless splitting of the torsional energy sublevels ($\Delta(4\text{–}1) \approx \Delta(3\text{–}2)$). The small rotational dependence of the torsional splitting was treated by utilizing two differing sets of Watson *S*-reduced rotational parameters, one for the upper torsional levels ($\tau = 3, 4$) and one for the lower levels ($\tau = 1, 2$). The rotational parameters determined by this effective analysis are listed in Table II. As can be seen from the residuals in Table I, the spectrum is fit well by this approach. An alternative method for analysis of the spectrum would be to utilize only one set of rotational parameters and treat the torsional-rotational Hamiltonian via the internal axis approach (IAM) of Hunt *et al.* (*1, 8*).

## III. THEORY AND ANALYSIS OF THE $^rQ_0$-BRANCH FREQUENCY DOUBLING

Here we discuss whether the perturbation approach to torsional doubling in the $v_s = 1$ state can account for the rotational dependence seen in the $^rQ_0$-branch transitions (Fig. 3). To incorporate rotational effects into Eq. (1), the rotational dependence of terms in both numerator and denominator must be investigated. Since the dominant

## TABLE I

Measured Frequencies for Rotational Transitions in the First Excited S–S Stretching State of HSSH

| J $K_a$ $K_c$ <- J $K_a$ $K_c$ | OBSERVED (MHZ) LOWER | OBSERVED (MHZ) UPPER | RESIDUAL (MHZ) [a] LOWER | RESIDUAL (MHZ) [a] UPPER |
|---|---|---|---|---|
| $^rP_0$-branch | | | | |
| 2 1 1 <- 3 0 3 | 98305.864 | | -0.0101 | |
| 4 1 3 <- 5 0 5 | 70602.995 | 70603.869 | 0.0215 | 0.0099 |
| 15 0 15 <- 14 1 13 | 67805.050 | 67804.170 | -0.0567 | -0.0710 |
| 20 0 20 <- 19 1 18 | 136914.397 | | -0.0763 | |
| 21 0 21 <- 20 1 19 | 150726.592 | | -0.0414 | |
| 22 0 22 <- 21 1 20 | 164535.155 | | -0.0862 | |
| 25 0 25 <- 24 1 23 | 205938.317 | | -0.0772 | |
| 27 0 27 <- 26 1 25 | 233520.230 | 233519.334 | -0.0137 | -0.0444 |
| 28 0 28 <- 27 1 26 | 247304.603 | | -0.0800 | |
| $^rQ_0$-branch | | | | |
| 1 1 1 <- 1 0 1 | 139867.503 | 139868.391 | -0.0233 | -0.0241 |
| 2 1 2 <- 2 0 2 | 139865.349 | 139866.224 | -0.0158 | -0.0297 |
| 3 1 3 <- 3 0 3 | 139862.104 | | -0.0181 | |
| 4 1 4 <- 4 0 4 | 139857.775 | 139858.651 | -0.0224 | -0.0352 |
| 5 1 5 <- 5 0 5 | 139852.369 | 139853.243 | -0.0208 | -0.0357 |
| 7 1 7 <- 7 0 7 | 139838.311 | 139839.185 | -0.0105 | -0.0256 |
| 8 1 8 <- 8 0 8 | 139829.609 | | -0.0489 | |
| 9 1 9 <- 9 0 9 | 139819.873 | 139820.766 | -0.0327 | -0.0290 |
| 10 1 10 <- 10 0 10 | 139809.048 | 139809.928 | -0.0149 | -0.0243 |
| 11 1 11 <- 11 0 11 | 139797.113 | 139798.020 | -0.0143 | 0.0032 |
| 13 1 13 <- 13 0 13 | 139769.932 | 139770.845 | -0.0355 | -0.0126 |
| 14 1 14 <- 14 0 14 | 139754.729 | 139755.614 | -0.0089 | -0.0143 |
| 15 1 15 <- 15 0 15 | 139738.409 | 139739.282 | 0.0046 | -0.0132 |
| 16 1 16 <- 16 0 16 | | 139721.841 | | -0.0138 |
| 17 1 17 <- 17 0 17 | 139702.312 | 139703.312 | -0.1000 | 0.0082 |
| 18 1 18 <- 18 0 18 | 139682.737 | 139683.604 | -0.0089 | -0.0343 |
| 19 1 19 <- 19 0 19 | 139661.941 | 139662.840 | -0.0202 | -0.0143 |
| 20 1 20 <- 20 0 20 | 139640.086 | 139640.942 | 0.0322 | -0.0056 |
| 21 1 21 <- 21 0 21 | 139617.031 | 139617.924 | 0.0119 | 0.0101 |
| 23 1 23 <- 23 0 23 | 139567.518 | 139568.426 | -0.0314 | -0.0203 |
| 24 1 24 <- 24 0 24 | 139541.079 | 139541.993 | -0.0253 | -0.0095 |
| 25 1 25 <- 25 0 25 | 139513.507 | 139514.426 | -0.0051 | 0.0144 |
| 26 1 26 <- 26 0 26 | 139484.761 | 139485.685 | -0.0061 | 0.0168 |
| 27 1 27 <- 27 0 27 | 139454.869 | 139455.787 | 0.0054 | 0.0206 |
| 28 1 28 <- 28 0 28 | | 139424.716 | | 0.0156 |
| 29 1 29 <- 29 0 29 | 139391.552 | 139392.469 | -0.0051 | 0.0052 |
| 30 1 30 <- 30 0 30 | 139358.134 | 139359.051 | -0.0073 | 0.0008 |
| 31 1 31 <- 31 0 31 | 139323.544 | 139324.465 | 0.0022 | 0.0119 |
| 32 1 32 <- 32 0 32 | 139287.767 | 139288.691 | 0.0154 | 0.0255 |
| 33 1 33 <- 33 0 33 | 139250.766 | 139251.712 | 0.0023 | 0.0317 |
| 34 1 34 <- 34 0 34 | 139212.561 | 139213.487 | -0.0096 | -0.0032 |
| 35 1 35 <- 35 0 35 | 139173.161 | 139174.095 | -0.0040 | 0.0073 |
| 36 1 36 <- 36 0 36 | 139132.545 | 139133.482 | 0.0061 | 0.0170 |
| 37 1 37 <- 37 0 37 | 139090.693 | 139091.637 | 0.0086 | 0.0229 |
| 38 1 38 <- 38 0 38 | 139047.576 | 139048.514 | -0.0173 | -0.0128 |
| 39 1 39 <- 39 0 39 | 139003.262 | 139004.217 | 0.0049 | 0.0224 |
| 41 1 41 <- 41 0 41 | | 138911.799 | | 0.0381 |
| 42 1 42 <- 42 0 42 | 138862.670 | 138863.623 | -0.0206 | -0.0183 |
| 43 1 43 <- 43 0 43 | 138813.300 | 138814.276 | 0.0147 | 0.0350 |
| 44 1 44 <- 44 0 44 | 138762.609 | 138763.484 | 0.0196 | -0.0662 |
| 45 1 45 <- 45 0 45 | 138710.595 | 138711.556 | 0.0019 | -0.0032 |
| 46 1 46 <- 46 0 46 | 138657.320 | 138658.302 | 0.0335 | 0.0440 |
| 47 1 47 <- 47 0 47 | 138602.666 | 138603.639 | 0.0068 | 0.0026 |
| 48 1 48 <- 48 0 48 | 138546.700 | 138547.692 | -0.0008 | 0.0081 |
| 49 1 49 <- 49 0 49 | 138489.400 | 138490.398 | -0.0006 | 0.0081 |
| 50 1 50 <- 50 0 50 | 138430.749 | 138431.751 | 0.0012 | 0.0077 |
| 51 1 51 <- 51 0 51 | 138370.727 | | -0.0042 | |
| 52 1 52 <- 52 0 52 | 138309.329 | 138310.342 | -0.0104 | -0.0059 |
| 53 1 53 <- 53 0 53 | 138246.555 | 138247.574 | -0.0059 | -0.0020 |
| 54 1 54 <- 54 0 54 | 138182.379 | | -0.0048 | |
| 55 1 55 <- 55 0 55 | 138116.783 | 138117.814 | -0.0131 | -0.0110 |
| 56 1 56 <- 56 0 56 | 138049.786 | 138050.820 | 0.0005 | -0.0016 |
| 57 1 57 <- 57 0 57 | 137981.326 | 137982.369 | -0.0136 | -0.0138 |
| 58 1 58 <- 58 0 58 | 137911.432 | 137912.484 | -0.0136 | -0.0120 |
| 59 1 59 <- 59 0 59 | 137840.082 | 137841.138 | -0.0086 | -0.0103 |
| 60 1 60 <- 60 0 60 | 137767.247 | 137768.305 | -0.0144 | -0.0214 |
| 61 1 61 <- 61 0 61 | | 137693.997 | | -0.0199 |
| 63 1 63 <- 63 0 63 | 137539.772 | 137540.856 | -0.0213 | -0.0242 |
| 64 1 64 <- 64 0 64 | 137460.942 | 137462.003 | 0.0111 | -0.0221 |
| 66 1 66 <- 66 0 66 | 137298.545 | 137299.655 | -0.0159 | -0.0143 |
| 67 1 67 <- 67 0 67 | 137215.106 | 137216.139 | 0.0821 | -0.0003 |
| 68 1 68 <- 68 0 68 | 137129.873 | 137131.099 | -0.0260 | 0.0777 |
| 69 1 69 <- 69 0 69 | 137043.156 | 137044.283 | -0.0149 | -0.0169 |
| 70 1 70 <- 70 0 70 | | 136955.944 | | -0.0156 |
| 71 1 71 <- 71 0 71 | 136864.832 | 136865.991 | -0.0109 | 0.0062 |
| 72 1 72 <- 72 0 72 | 136773.211 | 136774.354 | -0.0002 | -0.0054 |
| 73 1 73 <- 73 0 73 | 136679.889 | 136681.074 | -0.0240 | 0.0069 |

[a] Residual = Measured - Calculated Frequency

TABLE I—*Continued*

| $J\ K_a\ K_c$ <- $J\ K_a\ K_c$ | OBSERVED (MHZ) LOWER | OBSERVED (MHZ) UPPER | RESIDUAL (MHZ) [a] LOWER | RESIDUAL (MHZ) [a] UPPER |
|---|---|---|---|---|
| 74 1 74 <- 74 0 74 | 136584.924 | 136586.100 | -0.0077 | 0.0084 |
| 75 1 75 <- 75 0 75 | 136488.260 | | 0.0094 | |
| 76 1 76 <- 76 0 76 | 136389.842 | | -0.0109 | |
| 77 1 77 <- 77 0 77 | 136289.724 | | 0.0027 | |
| 78 1 78 <- 78 0 78 | 136187.852 | | 0.0134 | |
| 79 1 79 <- 79 0 79 | 136084.201 | | 0.0141 | |
| $^rR_0$-branch | | | | |
| 2 1 1 <- 1 0 1 | 167581.191 | 167582.079 | 0.0260 | 0.0259 |
| 5 1 4 <- 4 0 4 | 209153.458 | 209154.336 | -0.0578 | -0.0647 |
| 8 1 7 <- 7 0 7 | 250727.002 | 250727.884 | 0.0118 | 0.0140 |
| 14 1 13 <- 13 0 13 | 333863.506 | | 0.0212 | |
| $^rP_1$-branch | | | | |
| 6 2 5 <- 7 1 7 | | 322616.785 | | -0.0220 |
| 12 2 10 <- 13 1 12 | | 239388.977 | | -0.0597 |
| 12 2 11 <- 13 1 13 | | 239559.327 | | -0.0885 |
| 14 2 12 <- 15 1 14 | 211663.397 | 211664.279 | -0.0077 | -0.0472 |
| 14 2 13 <- 15 1 15 | 211888.952 | 211889.838 | -0.0132 | -0.0769 |
| 15 2 13 <- 16 1 15 | 197801.666 | 197802.564 | -0.0249 | -0.0468 |
| 15 2 14 <- 16 1 16 | 198057.896 | 198058.765 | -0.0083 | -0.0902 |
| 16 2 14 <- 17 1 16 | 183940.597 | | 0.0376 | |
| 16 2 15 <- 17 1 17 | 184229.548 | 184230.436 | 0.0533 | -0.0109 |
| 18 2 16 <- 19 1 18 | 156220.540 | 156221.435 | 0.0331 | 0.0114 |
| 18 2 17 <- 19 1 19 | 156581.274 | 156582.169 | 0.0656 | 0.0054 |
| 19 2 17 <- 20 1 19 | 142361.804 | 142362.689 | -0.0112 | -0.0423 |
| 19 2 18 <- 20 1 20 | 142761.613 | 142762.508 | -0.0103 | -0.0721 |
| 24 2 22 <- 25 1 24 | 73086.212 | 73087.105 | -0.0019 | -0.0282 |
| 24 2 23 <- 25 1 25 | 73715.200 | 73716.099 | 0.0071 | -0.0612 |
| 35 1 34 <- 34 2 32 | 65332.053 | 65331.152 | -0.0182 | 0.0409 |
| 35 1 35 <- 34 2 33 | 64059.412 | 64058.483 | 0.0045 | 0.0726 |
| 40 1 39 <- 39 2 37 | 134448.550 | | -0.0080 | |
| 40 1 40 <- 39 2 38 | 132748.362 | | -0.0243 | |
| 41 1 40 <- 40 2 38 | | 148261.803 | | -0.0361 |
| 41 1 41 <- 40 2 39 | 146467.727 | 146466.771 | -0.0038 | 0.0548 |
| 45 1 44 <- 44 2 42 | 203486.627 | 203485.701 | -0.0172 | 0.0624 |
| 45 1 45 <- 44 2 43 | 201278.061 | 201277.091 | -0.0032 | 0.0470 |
| 46 1 45 <- 45 2 43 | 217283.759 | 217282.823 | -0.0421 | 0.0266 |
| 46 1 46 <- 45 2 44 | 214963.010 | 214962.037 | -0.0324 | 0.0148 |
| 47 1 47 <- 46 2 45 | 228640.675 | 228639.678 | 0.0371 | 0.0596 |
| 48 1 47 <- 47 2 45 | 244866.857 | 244865.923 | -0.0523 | 0.0101 |
| 48 1 48 <- 47 2 46 | 242310.618 | 242309.633 | -0.0604 | -0.0276 |
| $^rQ_1$-branch | | | | |
| 9 2 8 <- 9 1 8 | | 419516.157 | | 0.0178 |
| 9 2 7 <- 9 1 9 | 419598.174 | 419599.230 | -0.0540 | 0.0578 |
| 10 2 9 <- 10 1 9 | 419501.412 | 419502.368 | 0.0239 | 0.0492 |
| 11 2 9 <- 11 1 11 | 419607.770 | 419608.757 | -0.0110 | 0.0308 |
| 12 2 11 <- 12 1 11 | 419469.669 | 419470.609 | 0.0117 | 0.0242 |
| 13 2 12 <- 13 1 12 | 419451.706 | 419452.768 | -0.0489 | 0.0872 |
| 14 2 13 <- 14 1 13 | 419432.523 | | 0.0216 | |
| 16 2 15 <- 16 1 15 | 419389.993 | 419390.922 | 0.0280 | 0.0346 |
| 17 2 15 <- 17 1 17 | 419646.746 | 419647.643 | 0.0045 | -0.0479 |
| 18 2 17 <- 18 1 17 | 419342.080 | 419343.027 | -0.0193 | 0.0063 |
| 19 2 18 <- 19 1 18 | 419316.165 | 419317.166 | -0.0208 | 0.0588 |
| 20 2 19 <- 20 1 19 | | 419289.931 | | 0.0469 |
| 20 2 18 <- 20 1 20 | 419671.770 | 419672.735 | 0.0397 | 0.0526 |
| 21 2 20 <- 21 1 20 | 419260.511 | 419261.371 | 0.0742 | 0.0115 |
| 21 2 19 <- 21 1 21 | 419680.859 | 419681.826 | 0.0293 | 0.0432 |
| 22 2 21 <- 22 1 21 | 419230.606 | 419231.565 | -0.0121 | 0.0227 |
| 22 2 20 <- 22 1 22 | 419690.321 | 419691.283 | 0.0202 | 0.0281 |
| 23 2 21 <- 23 1 23 | 419700.135 | 419701.113 | 0.0000 | 0.0228 |
| 24 2 23 <- 24 1 23 | 419167.122 | 419168.116 | -0.0160 | 0.0495 |
| 24 2 22 <- 24 1 24 | | 419711.328 | | 0.0484 |
| 25 2 23 <- 25 1 25 | | 419721.853 | | 0.0390 |
| 26 2 25 <- 26 1 25 | 419098.567 | 419099.565 | -0.0322 | 0.0308 |
| 27 2 26 <- 27 1 26 | 419062.423 | 419063.410 | -0.0358 | 0.0121 |
| 27 2 25 <- 27 1 27 | 419742.916 | 419743.905 | -0.0026 | 0.0264 |
| 28 2 27 <- 28 1 27 | 419025.001 | | -0.0848 | |
| 29 2 28 <- 29 1 28 | 418986.456 | 418987.431 | -0.0356 | -0.0094 |
| 29 2 27 <- 29 1 29 | 419766.247 | 419767.249 | 0.0077 | 0.0467 |
| 30 2 29 <- 30 1 29 | 418946.655 | 418947.662 | -0.0331 | 0.0196 |
| 31 2 30 <- 31 1 30 | 418905.646 | 418906.664 | -0.0417 | 0.0160 |
| 32 2 31 <- 32 1 31 | 418863.501 | 418864.459 | -0.0021 | -0.0106 |
| 34 2 33 <- 34 1 33 | 418775.692 | 418776.612 | 0.0579 | -0.0017 |
| 36 2 35 <- 36 1 35 | 418683.220 | 418684.215 | 0.0294 | 0.0317 |
| 36 2 34 <- 36 1 36 | 419856.443 | 419857.430 | -0.0159 | -0.0067 |
| 37 2 36 <- 37 1 36 | 418635.319 | | 0.0294 | |
| 37 2 35 <- 37 1 37 | 419870.249 | 419871.273 | -0.0240 | 0.0192 |

TABLE I—*Continued*

| $J\ K_a\ K_c$ <- $J\ K_a\ K_c$ | OBSERVED (MHZ) LOWER | OBSERVED (MHZ) UPPER | RESIDUAL (MHZ) [a] LOWER | RESIDUAL (MHZ) [a] UPPER |
|---|---|---|---|---|
| 38 2 37 <- 38 1 37 | | 418587.277 | | -0.0162 |
| 38 2 36 <- 38 1 38 | 419884.282 | 419885.246 | 0.0037 | -0.0164 |
| 39 2 37 <- 39 1 39 | 419898.429 | 419899.436 | -0.0315 | -0.0123 |
| 40 2 39 <- 40 1 39 | 418485.037 | 418486.030 | -0.0144 | -0.0341 |
| 41 2 40 <- 41 1 40 | 418432.830 | | -0.0166 | |
| 42 2 41 <- 42 1 41 | 418379.561 | 418380.600 | -0.0456 | -0.0224 |
| 43 2 42 <- 43 1 42 | 418325.373 | 418326.359 | 0.0245 | -0.0040 |
| 43 2 41 <- 43 1 43 | 419956.606 | 419957.661 | -0.0561 | -0.0080 |
| 44 2 43 <- 44 1 43 | 418270.054 | 418271.136 | -0.0357 | 0.0355 |
| 44 2 42 <- 44 1 44 | 419971.475 | 419972.468 | -0.0287 | -0.0486 |
| 45 2 44 <- 45 1 44 | 418213.789 | 418214.883 | -0.0591 | 0.0307 |
| 45 2 43 <- 45 1 45 | | 419987.465 | | 0.0155 |
| 46 2 45 <- 46 1 45 | 418156.670 | 418157.681 | 0.0282 | 0.0448 |
| 46 2 44 <- 46 1 46 | 420001.459 | 420002.434 | 0.0350 | -0.0171 |
| 47 2 46 <- 47 1 46 | 418098.479 | 418099.440 | -0.0106 | -0.0303 |
| 48 2 47 <- 48 1 47 | 418039.432 | 418040.465 | 0.0215 | 0.0919 |
| 48 2 46 <- 48 1 48 | 420031.464 | 420032.648 | -0.0850 | 0.0544 |
| 49 2 47 <- 49 1 49 | 420046.586 | 420047.673 | -0.0594 | -0.0271 |
| 51 2 49 <- 51 1 51 | 420076.829 | 420077.912 | 0.0116 | 0.0165 |
| 53 2 51 <- 53 1 53 | 420106.847 | 420107.991 | 0.0063 | 0.0440 |
| $^rP_2$-branch | | | | |
| 32 3 29 <- 33 2 31 | 242404.700 | 242405.623 | -0.0349 | -0.0378 |
| 32 3 30 <- 33 2 32 | 242337.755 | 242338.704 | -0.0349 | -0.0189 |
| 33 3 30 <- 34 2 32 | 228602.026 | 228602.956 | 0.0510 | 0.0530 |
| 33 3 31 <- 34 2 33 | 228526.728 | 228527.662 | 0.0485 | 0.0498 |
| 34 3 31 <- 35 2 33 | 214803.224 | 214804.141 | -0.0243 | -0.0374 |
| 34 3 32 <- 35 2 34 | 214718.846 | 214719.741 | -0.0004 | -0.0372 |
| 35 3 32 <- 36 2 34 | 201008.681 | 201009.681 | -0.0262 | 0.0413 |
| 35 3 33 <- 36 2 35 | 200914.398 | 200915.292 | -0.0010 | -0.0372 |
| 38 3 35 <- 39 2 37 | 159651.766 | 159652.698 | 0.0355 | 0.0270 |
| 38 3 36 <- 39 2 38 | 159522.486 | 159523.402 | 0.0390 | 0.0358 |
| 39 3 36 <- 40 2 38 | 145875.457 | 145876.389 | -0.0111 | -0.0225 |
| 39 3 37 <- 40 2 39 | 145732.576 | 145733.515 | -0.0395 | -0.0134 |
| 40 3 37 <- 41 2 39 | 132104.161 | | -0.0018 | |
| 56 2 54 <- 55 3 52 | 73762.947 | 73761.944 | 0.0506 | 0.0026 |

coupling with the $v_s = 1$ state involves the $v_t = 2$ state, the rotational effects discussed below are all based on this torsional state. To incorporate rotational dependence into the denominator of Eq. (1), one must simply include the rotational energies of the coupled states. Because the perturbation operator $\mathscr{H}'$ only connects the same rotational levels in the $v_s = 1$ and $v_t = 2$ vibrational states (*3*), the denominator becomes $E^{(0)}(v_s = 1) - E^{(0)}(v_t = 2) + E^{(0)}_{J,K}(v_s = 1) - E^{(0)}_{J,K}(v_t = 2)$, where $E^{(0)}_{J,K}$ is the rotational energy of either the upper state ($J$, $K = 1$) or the lower state ($J$, $K = 0$) of the $^rQ_0$-branch transitions, depending upon whether the torsional sublevel splitting $\Delta(3\text{–}2)$ ($K = 1$) or $\Delta(4\text{–}1)$ ($K = 0$) is being calculated. When rotational energy is included, the vibrational–rotational energy denominator is slightly different in the $\Delta(4\text{–}1)$ term from what it is in the $\Delta(3\text{–}2)$ term due to the difference in $K$ quantum number.

The rotational energy contribution in the denominators is given accurately for the near prolate top HSSH by the formula (*9*)

$$E^{(0)}_{J,K}(v_s = 1) - E^{(0)}_{J,K}(v_t = 2) \approx [\{(B + C)/2\}_{v_s=1} - \{(B + C)/2\}_{v_t=2}] \times J(J + 1) + [(A - (B + C)/2)_{v_s=1} - (A - (B + C)/2)_{v_t=2}] \times \{K^2 + 0.5b_pC_1\}, \quad (3)$$

where $A$, $B$, and $C$ are the well-known rotation constants, $b_p$ is the (very small) prolate asymmetry parameter, and $C_1$ is zero for $K = 0$ and $J(J + 1)/2$ for the (lower) $K = 1$ state accessible in $c$-type $^rQ_0$ transitions. The $J$-independent terms of Eq. (3) can be neglected in our analysis because they are far smaller than the vibrational energy

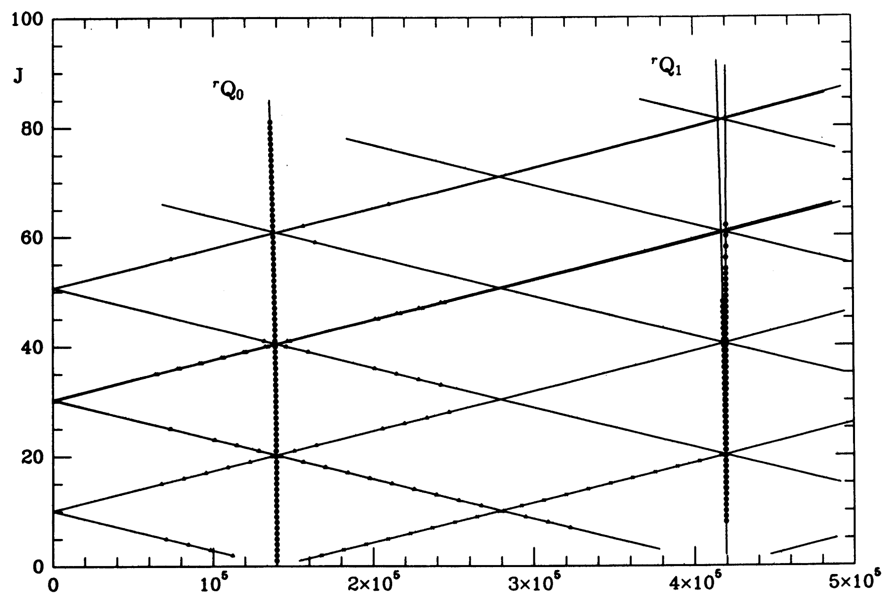


FIG. 1. A Fortrat diagram of the measured rotational transitions of the $v_s = 1$ state of HSSH.

difference and do not contribute to the measured $J$ dependence of $\Delta\nu$. Higher-order rotational terms (centrifugal distortion) are relatively unimportant through $J = 75$ in this context. The rotational constants $A$, $B$, and $C$ for the $v_s = 1$ state have been determined in this work (Table II), although the method of analysis utilized was to fit the rotational dependence of the frequency doublings with slightly different effective rotational constants for the upper ($\tau = 3, 4$) and lower ($\tau = 1, 2$) torsional states.

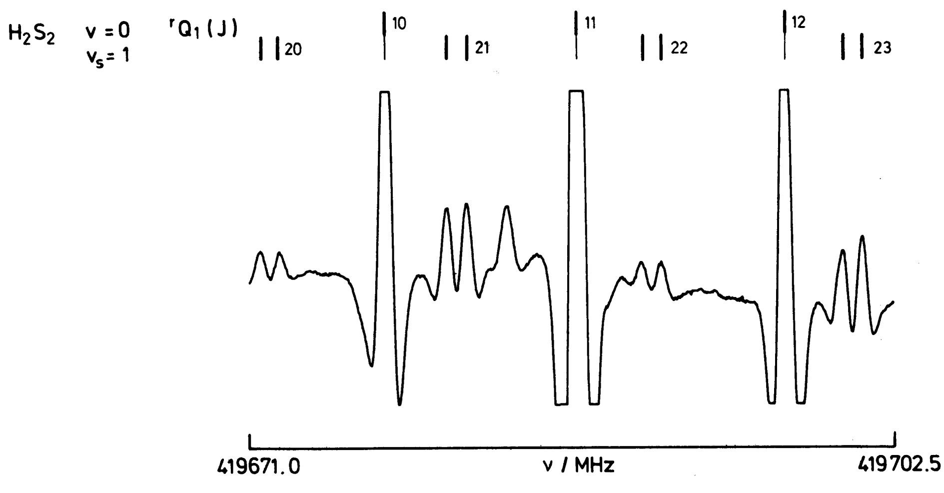


FIG. 2. A portion of the $^rQ_1$ branch of transitions of the $v_s = 1$ state of HSSH at 420 GHz. The actual transitions shown are the high frequency components of the $K$ doublets and have the quantum numbers $J_{2J-2} \leftarrow J_{1J}$.

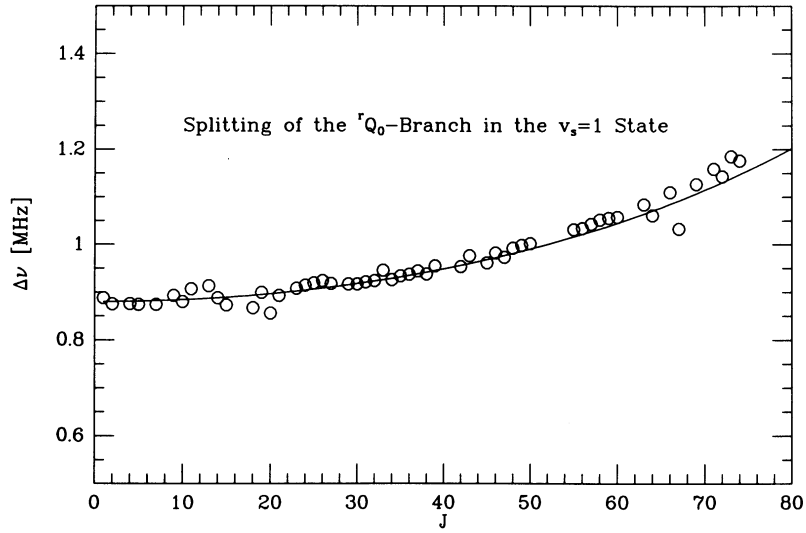


FIG. 3. The frequency doubling in the $v_s = 1$ state of HSSH measured in the $^rQ_0$-branch of rotational lines is plotted against $J$. The experimental points are given by the open circles while the theoretical prediction (see text) is given by the solid line.

Averaging these rotational constants and those obtained previously for $v_t = 2$ in a similar analysis (*1*), we obtain the rotational energy differences in Eq. (3) for $K = 0$ and $K = 1$ as functions of $J(J + 1)$. Because these differences are small compared with the vibrational energy difference between the $v_s = 1$ and $v_t = 2$ states, the denominators containing both vibrational and rotational energy terms can be expanded, leading to the previous results obtained for Δ(3–2) and Δ(4–1) with the exclusion of rotational energy multiplied by factors in the numerator of the second-order part of the expression for $\Delta\nu$ of $[1 + 4.75 \times 10^{-6} J(J + 1) + \cdots]$ for $K = 0$ and $[1 + 6.94 \times 10^{-6} J(J + 1) + \cdots]$ for $K = 1$. The average of these two factors will appear in the modified Eq. (1) because $\Delta(4\text{–}1) \approx \Delta(3\text{–}2)$ in the absence of rotation. This average factor—$1 + 5.85 \times 10^{-6} J(J + 1)$—is insufficient by itself to explain the measured rotational dependence of $\Delta\nu$ shown in Fig. 3, although it contains the measured "quadratic" rotational dependence which dominates the experimental measurement through $J = 75$ (see Eq. 2) and does increase with increasing $J$.

In addition to the rotational energy dependence of the denominator, one must consider the dependence in the numerator of Eq. (1). This will be dominated by the rotational dependence of $\Delta\nu^{(0)}_{v_t=2}$ since it is much larger than $\Delta v^{(0)}$ ($\Delta\nu^{(0)}_{v_t=2} \approx 750$ MHz, see below) and since the coupling matrix element will contain little if any rotational dependence since in the current theory the perturbation operator is a vibrational–torsional one only. The $J$ dependence of $\Delta\nu^{(0)}_{v_t=2}$ has been determined experimentally from the $^rQ_0$-branch series of lines up to $J = 23$ (*1*) and can be fit to the following expansion in $J(J + 1)$:

$$\Delta\nu^{(0)}_{v_t=2}(J) = 751.419 \text{ MHz} + 31.71 \text{ kHz } J(J + 1) + 1.31 \text{ Hz } [J(J + 1)]^2$$
$$= 751.419 \text{ MHz } \{1 + 4.22 \times 10^{-5} J(J + 1) + 1.74 \times 10^{-9} \times [J(J + 1)]^2\}. \quad (4)$$

TABLE II

Effective Spectroscopic Parameters[a,b]

| Parameter | Unit | Lower Torsional Levels ($\tau$ = 1,2) | Upper Torsional Levels ($\tau$ = 3,4) |
|---|---|---|---|
| A | MHz | 146799.077(11) | 146799.082(12) |
| B | MHz | 6928.53044(34) | 6928.53025(34) |
| C | MHz | 6926.67937(34) | 6926.67948(34) |
| $D_J$ | kHz | 5.41191(30) | 5.41186(30) |
| $D_{JK}$ | kHz | 77.6510(92) | 77.6408(84) |
| $D_K$ | MHz | 2.4241(45) | 2.4201(47) |
| $d_1$ | Hz | 9.766(19) | 9.853(20) |
| $d_2$ | Hz | -27.0985(88) | -27.119(10) |
| $H_J$ | mHz | -1.435(73) | -1.449(74) |
| $H_{JK}$ | mHz | 6.8(3.2) | 3.7(3.0) |
| $H_{KJ}$ | Hz | 85.0(1.1) | 84.0(1.0) |
| $H_K$ | kHz | -0.66(38) | -1.18(40) |
| $h_1$ | mHz | 0.0169(62) | -0.0083(63) |
| $h_2$ | mHz | 0.0430(41) | 0.0531(47) |
| $h_3$ | mHz | -0.0002(46) | 0.0066(33) |
| $\Delta\nu$ (J=0) | kHz | 879.836[c] | |

[a] These are obtained by incorporating the rotational dependence of the torsional doubling into the rotational and centrifugal distortion parameters.
[b] The figures in parenthesis represent one standard deviation and refer to the last digits of the parameters.
[c] This number is determined from the fit to the $^rQ_0$ torsional doublings and is not varied here.

The physical basis for the dominant dependence on $J(J+1)$ can be seen in the IAM (internal axis method) approach of Hunt *et al.* (*8*) in which there is a coupling with the correct $J(J+1)$ dependence between rotational–torsional levels differing in rotational quantum number $K$ by 1 and torsional quantum number $\tau$. The $J$ dependence in Eq. (4) can now be placed into the numerator of the modified Eq. (1). When coupled with the rotational dependence already determined from the energy denominator, we obtain a total dependence for the second-order term as a multiplicative factor $1 + (4.81 \times 10^{-5})J(J+1) + (1.99 \times 10^{-9})[J(J+1)]^2$. Thus

$$\Delta\nu^{(2)}(J) = \Delta\nu^{(2)}(J=0)\{1 + (4.81 \times 10^{-5})J(J+1) + (1.99 \times 10^{-9})[J(J+1)]^2\}, \quad (5)$$

where the calculated value of $\Delta\nu^{(2)}(J=0)$ is 1.90 MHz if only the $v_t = 2$ state is included in the perturbation calculation (*3*). Note that the lowest member of the split $^rQ_0$-branch series occurs for $J = 1$ and that $\Delta\nu^{(2)}(J=0)$ refers strictly to the second-order doubling calculated in the absence of rotation. The absolute size of the zeroth-order contribution to $\Delta\nu$ is small (0.15 MHz) and we ignore any rotational dependence that it possesses. Including this term, we obtain our final result that

$$\Delta\nu(J) = \Delta\nu(J=0)\{1 + (4.46 \times 10^{-5})J(J+1) + (1.84 \times 10^{-9})[J(J+1)]^2\}, \quad (6)$$

where $\Delta\nu(J=0)$ is 2.05 MHz.

The theoretical result is superimposed on the experimental plot of the doubling vs $J$ shown in Fig. 3 with $\Delta\nu$ ($J = 0$) set to the newly determined experimental result of 0.8798 MHz. It can be seen that the rotational dependence obtained via the perturbation treatment is perfectly adequate to explain the measured rotational dependence. This result is also noticeable in a comparison of the theoretically determined Eq. (6) with the experimental results in Eq. (2). Another, more accurate, manner of stating our results is that the experimental value of $\Delta\nu(J)$ divided by the theoretical value is pretty much independent of $J$ and equal to a factor of $\approx\frac{1}{2}$. This, in turn, shows that the probable error in the perturbation treatment lies in the $J$-independent matrix elements of the coupling operator (*3*). In any event, it would appear that the perturbation treatment given in Eq. (1) can be modified simply to explain the rotational dependence of the ${}^{r}Q_0$-branch frequency doubling caused by torsion in the $v_s = 1$ state over wide ranges of the rotational quantum number $J$. In addition, this paper and our previous one on the $v_s = 1$ state frequency doubling (*3*) show that spectroscopists should use caution in interpreting varying torsional splittings in different vibrational states in terms of different effective torsional potentials rather than in terms of coupling between vibrational states.

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