JOURNAL OF MOLECULAR SPECTROSCOPY **176,** 397–402 (1996)
ARTICLE NO. 0101

Anomalous *K*-Type Doubling of HSSH

Koichi M. T. Yamada,[1] Jörg Behrend, S. P. Belov, and Gisbert Winnewisser[2]

I. Physikalisches Institut, Universität zu Köln, 50937 Cologne, Germany

Received November 13, 1995; in revised form January 8, 1996

The anomalous *K*-type doubling observed in the millimeter- and submillimeter-wave spectra of HSSH in the $K_a = 2$ and 3 states is discussed by applying the second-order perturbation treatment to Watson's *S*-reduced Hamiltonian. The theory predicts that the anomaly does not occur for the levels $K_a \geqslant 4$. However, in the present observation, it was not possible to resolve the *K*-doublets in the $^rQ_4$ transitions, and the experimental proof for this prediction is left for future studies.

I. INTRODUCTION

Disulfane (HSSH) is known as the first and probably most conspicuous example where the anomalous *K*-type doubling for the $K_a = 2$ rotational levels has been detected; the energy of the E^+ component is lower than that of E^- component, which was discovered by millimeter-wave (mmW) spectroscopy during the years 1968–1972 (*1*). The very small inertial asymmetry of HSSH contributes to the *K*-type doubling of the $K_a = 2$ level much less than the effect of centrifugal distortion by the $\Delta K = \pm 4$ off-diagonal matrix elements, resulting in a reversal of the energy order of the doublet components. This anomalous *K*-type doubling is clearly observable by high resolution spectroscopy. The nuclear-spin statistics, associated with the C_2 symmetry of the molecule, leads to the unambiguous assignments of the *K*-doublet components. Without this additional assignment criterion, it would be hard to distinguish the two components, and thus consequently it would be very difficult to unambiguously conclude the existence of the anomaly.

The anomalous *K*-doubling entrusts a special significance to Watson's *S*-reduced Hamiltonian (*2*), because it can reproduce the anomaly which can not be expected by the *A*-reduced Hamiltonian, since it does not contain the $\Delta K = \pm 4, \pm 6, \cdots$ off-diagonal elements. A summary of the previous work concerning this molecule is given in Ref. (*3*) where the spectroscopic literature published before 1990 is listed. Recently, we developed a high-precision sub-mmW spectrometer based on backward wave oscillators (BWO) made in Russia, and observed the $^rQ_2$ and $^rQ_3$ transitions, near 700 and 980 GHz, respectively (*4, 5*). The analysis of the observed spectra of the $^rQ_3$ transitions revealed that the *K*-type doubling for the $K_a = 3$ is also anomalous; the $K_a + K_c = J$ level is lower in energy than the $K_a + K_c = J + 1$ level for $K_a = 3$.

This paper presents our most recent sub-mmW measurements on the $^rQ_4$ transitions of HSSH near 1.2 THz (*6*), together with the spectrum of the $^rQ_2$ transitions which have been remeasured near 700 GHz, with improved signal-to-noise ratio and with flat base lines. It should however be noted that the *J*-pattern of the $^rQ_4$ branch has been measured up to $J = 46$. For this *J* value, no *K*-splitting is observed. The analytical forms for predicting the *K*-type doublings for various K_a have been derived from Watson's *S*-reduced Hamiltonian using the second-order perturbation method.

II. THEORETICAL CONSIDERATIONS AND OBSERVED SPECTRA

In this section, the anomalous *K*-doubling effect found in HSSH is explained by means of the standard second order perturbation theory. Watson's *S*-reduced Hamiltonian up to sextic terms, which is appropriate for HSSH, is

$$\begin{aligned}\hat{H} = {} & \frac{1}{2}(B + C)\hat{J}^2 + \left\{A - \frac{1}{2}(B + C)\right\}\hat{J}_z^2 - D_J\hat{J}^4 \\ & - D_{JK}\hat{J}^2\hat{J}_z^2 - D_K\hat{J}_z^4 + H_J\hat{J}^6 + H_{JK}\hat{J}^4\hat{J}_z^2 + H_{KJ}\hat{J}^2\hat{J}_z^4 \\ & + H_K\hat{J}_z^6 + \frac{1}{4}(B - C)(\hat{J}_+^2 + \hat{J}_-^2) + d_1\hat{J}^2(\hat{J}_+^2 + \hat{J}_-^2) \\ & + d_2(\hat{J}_+^4 + \hat{J}_-^4) + h_1\hat{J}^4(\hat{J}_+^2 + \hat{J}_-^2) + h_2\hat{J}^2(\hat{J}_+^4 + \hat{J}_-^4) \\ & + h_3(\hat{J}_+^6 + \hat{J}_-^6).\end{aligned} \quad [1]$$

The discussion is limited here to near prolate asymmetric rotors. Among the operators in the Hamiltonian, those which are responsible for the *K*-type doubling can be reorganized in the following three parts:

[1] Present address: National Institute for Interdisciplinary Research (NAIR), Tsukuba, Ibaraki 305, Japan.

[2] E-mail: winnewisser@ph1.uni-koeln.de.

0022-2852/96 $18.00

TABLE 1
Energy Matrix for $J = 7$[a]

$E^{\pm}$	0	2	4	6
$K_a = 0$	E_0	$\sqrt{2}W_{02}$	$\sqrt{2}V_{04}$	0
2	$\sqrt{2}W_{02}$	$E_2 \pm V_{2-2}$	W_{24}	V_{26}
4	$\sqrt{2}V_{04}$	W_{24}	E_4	W_{46}
6	0	V_{26}	W_{46}	E_6
$O^{\pm}$	1	3	5	7
$K_a = 1$	$E_1 \pm W_{1-1}$	$W_{13} \pm V_{1-3}$	V_{15}	0
3	$W_{13} \pm V_{1-3}$	E_3	W_{35}	V_{37}
5	V_{15}	W_{35}	E_5	W_{57}
7	0	V_{37}	W_{57}	E_7

[a] For E^-, the row and column of $K_a = 0$ do not exist.

$$\hat{H}_2 = \left\{\frac{1}{4}(B - C) + d_1\hat{J}^2 + h_1\hat{J}^4\right\}(\hat{J}_+^2 + \hat{J}_-^2) \qquad [2]$$

$$\hat{H}_4 = (d_2 + h_2\hat{J}^2)(\hat{J}_+^4 + \hat{J}_-^4) \qquad [3]$$

$$\hat{H}_6 = h_3(\hat{J}_+^6 + \hat{J}_-^6). \qquad [4]$$

Here $\hat{H}_n$ represents the $\Delta K_a = \pm n$ interaction terms. For the present discussion, it is sufficient to consider only the leading term of the $\hat{H}_n$; the contributions of these terms are expected in general to be much more significant than those of d_1, h_1, and h_2 terms, as is in the case for HSSH. The off-diagonal matrix elements in the symmetric top basis $|J, k\rangle$ are then calculated to be

$$W_{k,k\pm2} = \langle J, k|\hat{H}_2|J, k \pm 2\rangle$$
$$= \frac{1}{4}(B - C)f(J, k, k \pm 2) \qquad [5]$$

$$V_{k,k\pm4} = \langle J, k|\hat{H}_4|J, k \pm 4\rangle$$
$$= d_2 f(J, k, k \pm 2) f(J, k \pm 2, k \pm 4) \qquad [6]$$

$$U_{k,k\pm6} = \langle J, k|\hat{H}_6|J, k \pm 6\rangle$$
$$= h_3 f(J, k, k \pm 2) f(J, k \pm 2, k \pm 4) \times f(J, k \pm 4, k \pm 6), \qquad [7]$$

where

$$f(J, k, k \pm 2) = \sqrt{\{J(J + 1) - k(k \pm 1)\}\{J(J + 1) - (k \pm 1)(k \pm 2)\}}. \qquad [8]$$

By substituting the values $B - C \approx 3$ MHz, $d_2 \approx -27$ Hz, and $h_3 \approx 3.4$ μHz, which are close to the actual numbers for HSSH, we can estimate the order of magnitude of these matrix elements; in the case of HSSH, for $J = 60$ they are

$$W_{k,k\pm2} \approx 2745 \text{ MHz} \qquad [9]$$

$$V_{k,k\pm4} \approx -362 \text{ MHz} \qquad [10]$$

$$U_{k,k\pm6} \approx 0.17 \text{ MHz}. \qquad [11]$$

The energy matrix, block diagonalized in the basis of the Wang linear combinations, is listed in Table 1 with the diagonal elements, E_K and off-diagonal matrix elements, W and V defined above, where the terms of $U(\Delta K = \pm6)$ are neglected for HSSH because of their small order of magnitude as shown in Eq. [11].

The $K_a = 2$ Doublet

Following the second-order perturbation theory, the eigen value ϵ_2^+ for $K_a = 2$ of the E^+ matrix and ϵ_2^- of the E^- matrix are

$$\epsilon_2^+ = E_2 + V_{2,-2} + \frac{2|W_{0,2}|^2}{E_2 + V_{2,-2} - E_0} + \frac{|W_{2,4}|^2}{E_2 + V_{2,-2} - E_4} + \frac{|W_{2,6}|^2}{E_2 + V_{2,-2} - E_6} \qquad [12]$$

$$\epsilon_2^- = E_2 - V_{2,-2} + \frac{|W_{2,4}|^2}{E_2 - V_{2,-2} - E_4} + \frac{|W_{2,6}|^2}{E_2 - V_{2,-2} - E_6}. \qquad [13]$$

In the rigid-rotor approximation where the $V_{2,-2}$ term vanishes, the difference between these two eigenvalues depends solely on the term of $W_{0,2}$ and

$$\epsilon_2^+ - \epsilon_2^- = \frac{2|W_{0,2}|^2}{E_2 - E_0} > 0; \qquad [14]$$

thus it is obvious from these equations that $\epsilon_2^+ > \epsilon_2^-$. We call this ordering of the K-doublet as *normal* doublet, which is caused by the inertial asymmetry. This relation holds also for the case $V_{2,-2} > 0$; i.e., we expect *normal* doublet for $V_{2,-2} \geqslant 0$.

However, in the case of HSSH, $V_{2,-2} < 0$ as given in Eq. [10], the difference in the eigenvalues is

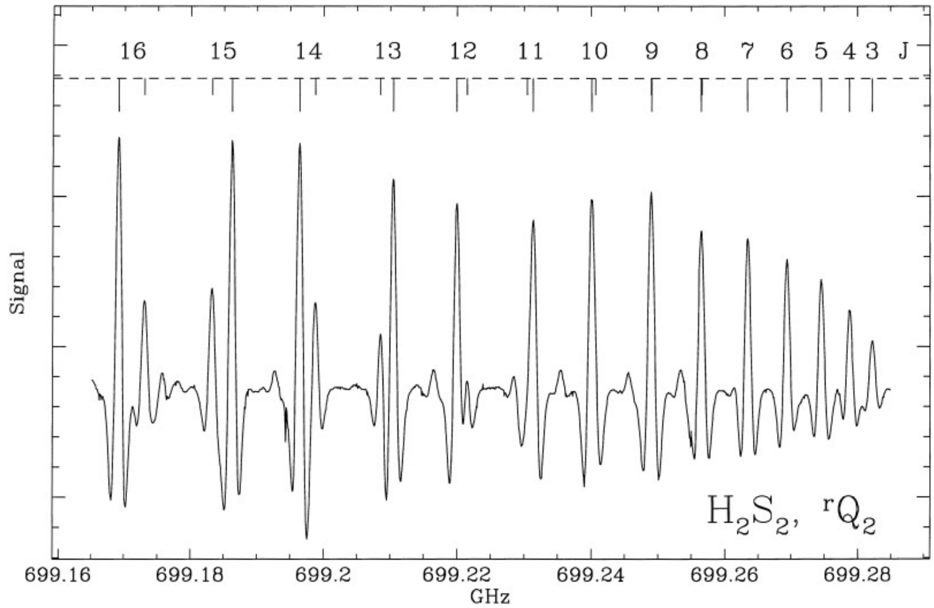

FIG. 1. Band head of the $^rQ_2$ branch of HSSH with observed anomalous K-splitting. The J assignments have been made by counting the lines from the band head. For all transitions with $J \geqslant 12$, the splitting is resolved and the observed intensity alternation labels the appropriate energy levels. The observed intensity pattern is reversed as compared to predictions based solely on the inertial splitting. The apparent decrease of intensities for J = 10, 11, 12, and 13 are caused by the line broadening due to the partially resolved K-doublet; the second derivative signal decreases for broader lines.

$$\epsilon_2^+ - \epsilon_2^- = 2V_{2,-2} + \frac{2|W_{0,2}|^2}{E_2 - E_0}, \qquad [15]$$

where the contribution of $V_{2,-2}$ in the denominators are neglected. For the $J = 60$ level of HSSH, the contribution of the first term is about −700 MHz and of the second term 27 MHz. Therefore the K-doublet is inverted for the K_a = 2 level of HSSH. We call this as *anomalous* doublet.

In fact, the K-type splittings have been observed in the c-type $^rQ_2$ transitions of HSSH, as shown in Fig. 1. The clearly observed intensity alternation leads us to an unambiguous assignment for the K_c quantum number; the levels of odd K_c are three times more weighted than the levels of even K_c. For example, the lower state quantum numbers of the $^rQ_2(14)$ transition are $14_{2,12}$ or $14_{2,13}$. Following the spin statistics, the stronger component (low frequency component in this case) have to be assigned to the transition of $K_c = 13$, and the weaker component (high frequency component) to $K_c = 12$.

Thus, from this figure we can conclude that, for a given J, the Q-branch line from the level with $K_a + K_c = J$ is higher in frequency than that from the level with $K_a + K_c = J + 1$. Since the K-type doubling in the $K_a = 3$ state is much smaller than that in the $K_a = 2$, the observed splittings in these Q-branch transitions reflect directly the fact that the energy of the K-type doubling component of $K_a + K_c = J$, which corresponds to ϵ^+ in Eq. [12], is lower than that of $K_a + K_c = J + 1$, which is ϵ^- in Eq. (13); i.e., the anomalous K-type doubling is observed for the $K_a = 2$ state of HSSH.

The K_a = 3 Doublet

Similarly, the eigenvalues for the K_a = 3 levels of O^+ and O^- matrix are

$$\epsilon_3^+ = E_3 + \frac{|W_{1,3} + V_{1,-3}|^2}{E_3 - (E_1 + W_{1,-1})} + \frac{|W_{3,5}|^2}{E_3 - E_5} + \frac{|V_{3,7}|^2}{E_3 - E_7} \qquad [16]$$

$$\epsilon_3^- = E_3 + \frac{|W_{1,3} - V_{1,-3}|^2}{E_3 - (E_1 - W_{1,-1})} + \frac{|W_{3,5}|^2}{E_3 - E_5} + \frac{|V_{3,7}|^2}{E_3 - E_7}. \qquad [17]$$

The difference,

$$\epsilon_3^+ - \epsilon_3^- = \frac{|W_{1,3} + V_{1,-3}|^2}{E_3 - (E_1 + W_{1,-1})} - \frac{|W_{1,3} - V_{1,-3}|^2}{E_3 - (E_1 - W_{1,-1})}, \qquad [18]$$

is positive in the rigid-rotor approximation ($V_{1,-3} = 0$) because of the difference in the denominator,

$$E_3 - (E_1 + W_{1,-1}) < E_3 - (E_1 - W_{1,-1}). \qquad [19]$$

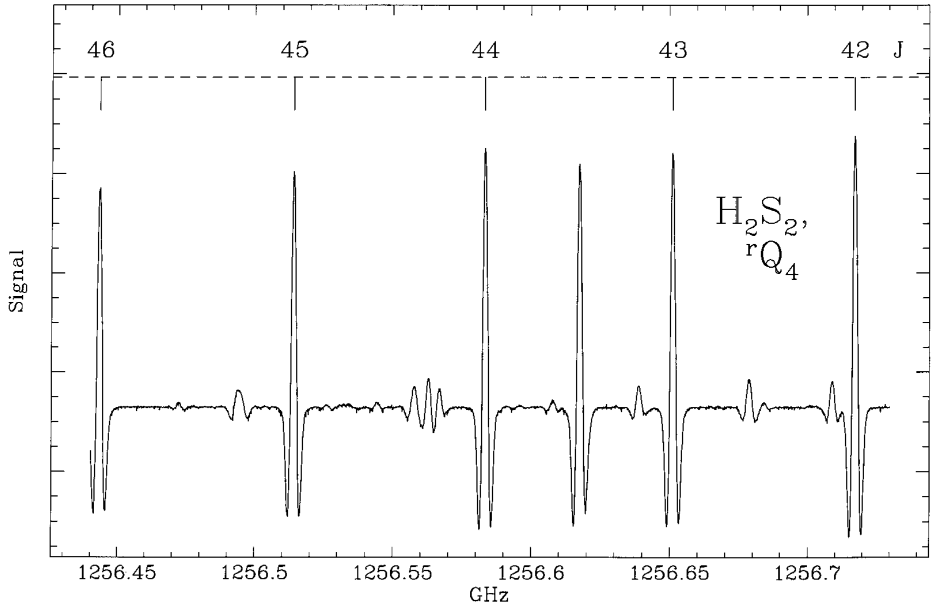

FIG. 2. High-J transitions of the $^rQ_4$ branch. As predicted, the K-doubling is too small to be resolved. For $J \sim 90$ a small splitting (~3 MHz) should become observable. It is expected to be normal; i.e., the high frequency component of an even J transition should be three times more intense, because the $J_{4,J-3}$ level carries statistical weight 3 and $J_{4,J-4}$ has weight 1 for even J.

The same is true for $V_{1,-3} > 0$, since all W terms are positive as given in Eq. [5] for HSSH. Thus for $V_{1,-3} \geqslant 0$, we expect *normal* doublet for $K_a = 3$.

In the case of $V_{1,-3} < 0$ more careful evaluation of the contributions from each term is required. Equation [18] may be rewritten as

$$\epsilon_3^+ - \epsilon_3^- = \left\{\frac{|W_{1,3}|^2 + |V_{1,-3}|^2}{E_3 - (E_1 + W_{1,-1})} - \frac{|W_{1,3}|^2 + |V_{1,-3}|^2}{E_3 - (E_1 - W_{1,-1})}\right\} + \left\{\frac{2W_{1,3}V_{1,-3}}{E_3 - (E_1 + W_{1,-1})} + \frac{2W_{1,3}V_{1,-3}}{E_3 - (E_1 - W_{1,-1})}\right\}. \quad [20]$$

The first block of the equation above contributes to the *normal* doubling which originates from the difference in the denominator, and the second part contributes to the *anomalous* doubling. For $J = 60$ of HSSH, the former contribution is less than 100 kHz whereas the latter is about -3 MHz. Thus the $K_a = 3$ doublet of HSSH is anomalous. It should be noted that this anomaly in the $K_a = 3$ level is enhanced by the inertial asymmetry term $W_{1,3}$. The neglected sextic term, $U_{-3,3}$, contributes to this splitting approximately by 0.34 MHz for $J = 60$, which is one order of magnitude smaller than the value given above. However, in the cases where the parameter h_3 is larger or where the interested J is much larger than in the present case, we have to take the contribution of $U_{-3,3}$ into account for $K_a = 3$ splittings.

The observed spectra of the $^rQ_3$ transitions have been published in our previous paper (*5*); in particular the region where the K-type splittings has been resolved is shown in Fig. 4 of Ref. (*5*). Exactly the same discussion given for the $^rQ_2$ transitions is valid also here, and the anomalous K-type doubling has been found for the $K_a = 3$ state of HSSH.

The $K_a = 4$ Doublet

The eigenvalues for the $K_a = 4$ levels of E^+ and E^- matrix are

$$\epsilon_4^+ = E_4 + \frac{2|V_{0,4}|^2}{E_4 - E_0} + \frac{|W_{2,4}|^2}{E_4 - (E_2 + V_{2,-2})} + \frac{|W_{4,6}|^2}{E_4 - E_6} + \frac{|V_{4,8}|^2}{E_4 - E_8} \quad [21]$$

$$\epsilon_4^- = E_4 + \frac{|W_{2,4}|^2}{E_4 - (E_2 - V_{2,-2})} + \frac{|W_{4,6}|^2}{E_4 - E_6} + \frac{|V_{4,8}|^2}{E_4 - E_8}. \quad [22]$$

Again neglecting the $V_{2,-2}$ contribution in the denominators, the difference in the eigenvalues is

$$\epsilon_4^+ - \epsilon_4^- = \frac{2|V_{0,4}|^2}{E_4 - E_0} > 0. \quad [23]$$

Thus in general we expect again *normal* doublet in $K_a = 4$. The doublet splitting for $J = 60$ of HSSH is then predicted to be about 0.12 MHz, which is very small. Figure 2 shows the high-J transitions, observed so far, of the $^rQ_4$ branch. As predicted, no indication of the K-splitting is observed. In order to resolve the doublet, we have to measure transitions with $J > 80$ in Doppler-limited spectra, or we have to measure with sub-Doppler resolution, which has recently been demonstrated to be possible in our sub-mmW spectrometer with NH_3 (*7*).

TABLE 2
Observed and Calculated Frequencies of $^rQ_4$ Transitions of HSSH in the Ground Vibrational State[a]

J	Observed	Calculated	O–C
5	1258083.2536	1258083.1017	0.1518 *b*
6	1258073.8800	1258073.8797	0.0004
7	1258063.1227	1258063.1205	0.0022
8	1258050.7985	1258050.8241	−0.0257
9	1258037.0030	1258036.9905	0.0125
10	1258021.6450	1258021.6196	0.0254
11	1258004.7076	1258004.7113	−0.0037
12	1257986.2716	1257986.2655	0.0061
13	1257966.2839	1257966.2822	0.0017
14	1257944.7684	1257944.7611	0.0072
15	1257921.7528	1257921.7023	0.0504
16	1257897.1141	1257897.1056	0.0086
17	1257870.9609	1257870.9708	−0.0100
18	1257843.2616	1257843.2979	−0.0363
19	1257814.0912	1257814.0867	0.0045
20	1257783.3034	1257783.3370	−0.0337
21	1257751.1412	1257751.0487	0.0925 *b*
22	1257717.2294	1257717.2217	0.0077
23	1257681.8136	1257681.8557	−0.0421
24	1257644.9602	1257644.9505	0.0096
25	1257606.4662	1257606.5061	−0.0399
26	1257566.5186	1257566.5221	−0.0035
27	1257525.0233	1257524.9984	0.0249
28	1257481.9856	1257481.9348	0.0509
29	1257437.3277	1257437.3310	−0.0033
30	1257391.1888	1257391.1868	0.0020
31	1257343.5151	1257343.5020	0.0131
32	1257294.2897	1257294.2764	0.0133
33	1257243.4775	1257243.5096	−0.0321
34	1257191.1947	1257191.2014	−0.0067
35	1257137.3562	1257137.3517	0.0045
36	1257081.9195	1257081.9599	−0.0405
37	1257025.0173	1257025.0260	−0.0087
38	1256966.5400	1256966.5496	−0.0096
39	1256906.5332	1256906.5304	0.0028
40	1256844.9807	1256844.9681	0.0127
41	1256781.8603	1256781.8623	−0.0020
42	1256717.2034	1256717.2129	−0.0094
43	1256651.0024	1256651.0193	−0.0169
44	1256583.2737	1256583.2814	−0.0077
45	1256514.0079	1256513.9987	0.0092
46	1256443.1817	1256443.1709	0.0108

[a] All numbers in MHz.
[b] Not included in the fit.

TABLE 3
Revised Ground State Constants of HSSH[a]

Parameter	Value	Unit
A	146 858.2000(39)	MHz
B	6 970.42822(49)	MHz
C	6 967.68727(48)	MHz
D_J	5.39995(50)	kHz
D_{JK}	85.5267(27)	kHz
D_K	2.44021(66)	MHz
d_1	9.0080(44)	Hz
d_2	−27.33792(87)	Hz
H_J	−1.43(15)	mHz
H_{JK}	−22.12(36)	mHz
H_{KJ}	3.27(21)	Hz
H_K	0.385(43)	kHz
h_2	41.62(15)	μHz
h_3	3.446(33)	μHz
L_{JK}	0.230(16)	mHz
L_{KJ}	−4.5(47)	mHz
L_K	0.38(90)	Hz

[a] The numbers in parentheses are one standard deviation in units of the last digit quoted.

The $K_a = 5$ Doublet

The eigenvalues for the $K_a = 5$ levels of O^+ and O^- matrix are

$$\epsilon_5^+ = E_5 + \frac{|V_{1,5}|^2}{E_5 - (E_1 + W_{1,-1})} + \frac{|W_{3,5}|^2}{E_5 - E_3} + \frac{|W_{5,7}|^2}{E_5 - E_7} + \frac{|V_{5,9}|^2}{E_5 - E_9} \quad [24]$$

$$\epsilon_5^- = E_5 + \frac{|V_{1,5}|^2}{E_5 - (E_1 - W_{1,-1})} + \frac{|W_{3,5}|^2}{E_5 - E_3} + \frac{|W_{5,7}|^2}{E_5 - E_7} + \frac{|V_{5,9}|^2}{E_5 - E_9}. \quad [25]$$

The difference in the eigenvalues is

$$\epsilon_5^+ - \epsilon_5^- = \frac{|V_{1,5}|^2}{E_5 - (E_1 + W_{1,-1})} - \frac{|V_{1,5}|^2}{E_5 - (E_1 - W_{1,-1})} > 0. \quad [26]$$

Thus *normal* K-doublet is expected for $K_a = 5$ in general. The amount of this splitting at $J = 60$ of HSSH is predicted to be negligibly small.

III. SUMMARY

The second-order perturbation theory predicts (up to the quartic centrifugal distortion effect) that:

1. the K-doublet is *normal* for $K_a \geqslant 4$ in any case;
2. the K-doublet for all K_a value is in general *normal* if $d_2 \geqslant 0$; and
3. the K-doublet may be *anomalous* for $K_a = 2$ and 3 if $d_2 < 0$.

The energy term values of HSSH belong to case 3, and we have observed the anomalous K-type doubling for both $K_a = 2$ and 3 rotational levels.

In the above discussion, we used second-order perturbation theory. For high-K states, higher-order corrections are important and should be evaluated more carefully. However, the second-order predictions given above are confirmed by the numerical diagonalization of the energy matrix for HSSH. In adding the newly observed line positions of ${}^rQ_4$ transitions listed in Table 2 to the previously available mmW and sub-mmW data (*8*), we have revised the ground state constants as listed in Table 3. An exact frequency prediction with the newly obtained parameters indicates that the K-type splitting of the ${}^rQ_4$ transition is expected to be 0.115 MHz for $J = 60$, 1.12 MHz for $J = 80$, and 2.85 MHz for $J = 90$.

The phenomena discussed in this paper are also observed in DSSD and possibly in HSSD. In the case of HSSD, an asymmetrically substituted isotopomer, the discussion should be based on very careful fittings of the observed line frequencies, because the additional information from the nuclear spin statistics is missing.

Recently, Wagener *et al.* (*9*) discovered that the K-doubling of HNCNH is anomalous for $K_a = 2$ by observing the ${}^rQ_2$ transitions. In this case, the transitions are of b-type. As far as we know, the anomalous K-type doubling is observed only for these two molecules.

ACKNOWLEDGMENTS

The author thanks F. Lewen and Th. Klaus for their help in measuring sub-mmW spectra. This work is supported in part by Special Grant SFB-301 by the Deutsche Forschungsgemeinschaft (DFG) via Grant SFB 301 and special funding from the Science Ministry of the State Nordrhein-Westfalen. The stay of S.P.B. in Cologne has been made possible by the DFG through grants aimed to support Eastern and Central European Countries and the Republics of the former Soviet Union.

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