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LETTER TO THE EDITOR

The $^rQ_3$ Branch of HSSH at 980 GHz: Anomalous K-Doubling of the K_a = 3 Levels

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In collaboration with our colleagues from the Institute of Applied Physics, Nizhnii Novgorod, Russia, we have opened the Terahertz frequency region for high-resolution spectroscopy in our Cologne laboratory. As a first example, we present spectra of the ground state $^rQ_3$ branch of HSSH, whose band center lies just below 1 THz. The entire Q branch, including the Q branches of the first and second excited torsional states, have been observed using the fundamental radiation of a high-frequency backward wave oscillator.

High-resolution rotational spectra of disulfane, HSSH, have been reported in a long series of papers (*1*), commencing in 1968 and 1972 with the detection of the pure rotational transitions of the $^rQ_0$ branch at 139.9 GHz (*2*) and the $^rQ_1$ branch at 419.6 GHz (*3*), respectively. Due to its skew chain structure, HSSH is a very nearly symmetric prolate top and exhibits a perpendicular-type spectrum, whose main characteristics are the regularly spaced, fairly intense Q branches with closely packed J components. The frequency positions of these c-type Q-branch heads and the present experimental situation, as far as measurements are concerned, are summarized in Fig. 1. It shows that so far only the lowest two Q branches have been observed by

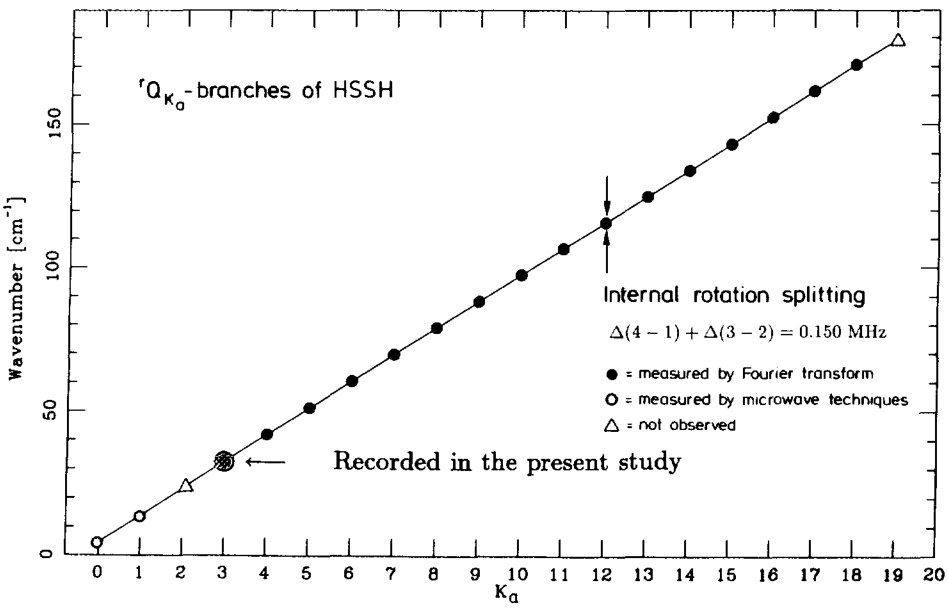

FIG. 1. $^rQ_{K_a}$ branches of HSSH. Plot of the bandhead position of the Q branches vs the lower K_a value. The $^rQ_3$ branch has previously been recorded with FTIR spectroscopy, but here for the first time with microwave techniques.

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microwave techniques, whereas the others, commencing with the $^rQ_3$ branch, have been recorded by Fourier-transform infrared spectroscopy. The $^rQ_2$ branch near 700 GHz has not been seen by either technique.

By using our submillimeter-wave spectrometer (*4*) and replacing in its experimental arrangement the radiation sources with a high-frequency backward wave oscillator, we have been able to record the $^rQ_3$ branch of HSSH. The Russian backward wave oscillator is presently operated in the free running mode and the recorded spectra give an impression of its wide and fine tuning capability. In Fig. 2 the obtained HSSH spectrum is compared with that from FTIR spectroscopy. The bandhead region is shown in Fig. 3 in an expanded scale. As expected from our highly precise frequency predictions (*5*), the features of the $^rQ_3$-branch head are overlapped by the bandhead of $HS^{34}SH$, which appears displaced at slightly higher frequencies than the bandhead of the main isotope species. Both Q branches are degraded to lower frequencies and do not exhibit resolvable splitting for low and medium J. Consequently, these Q-branch lines of the symmetric main isotopomer $H^{32}S^{32}SH$ do not show the 3:1 intensity alternation for low and medium J values which is expected from the nuclear spin statistics of the hydrogen nuclei ($I = \frac{1}{2}$). The K-doublet components of the same J transition coincide and thus the intensity of the different J lines just follow the Boltzmann distribution (see Fig. 2).

However, this situation changes for high J values ($J \sim 60$), where the expected K-doubling becomes resolvable and the 3:1 intensity alternation visible. In HSSH the sequence of the intensity alternation is of particular interest for the $^rQ_3$ branch. It has been well established for HSSH and DSSD (*3, 6*) that the K-type doubling in molecules with very small asymmetry is caused by two effects: a splitting due to the $\Delta K = \pm 2$ matrix elements originating from the inertial asymmetry, the *asymmetry splitting*, and a *centrifugal*

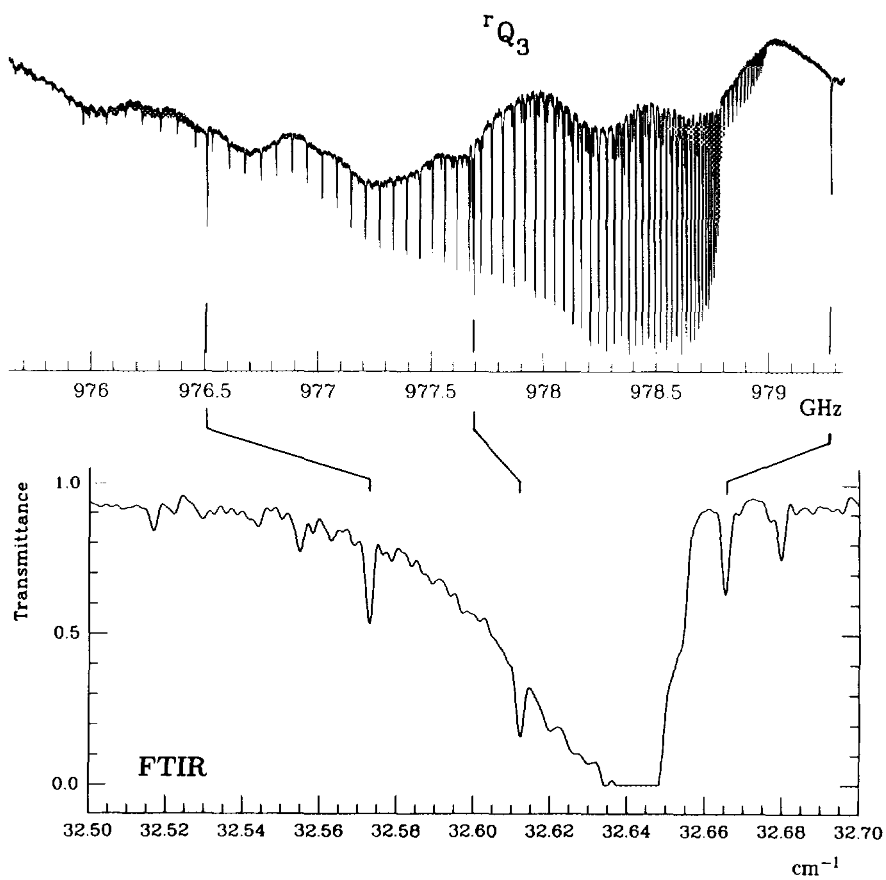

FIG. 2. Survey scan of H_2S_2 over the complete $^rQ_3$ region and comparison with the FTIR recording obtained in the Giessen laboratory.

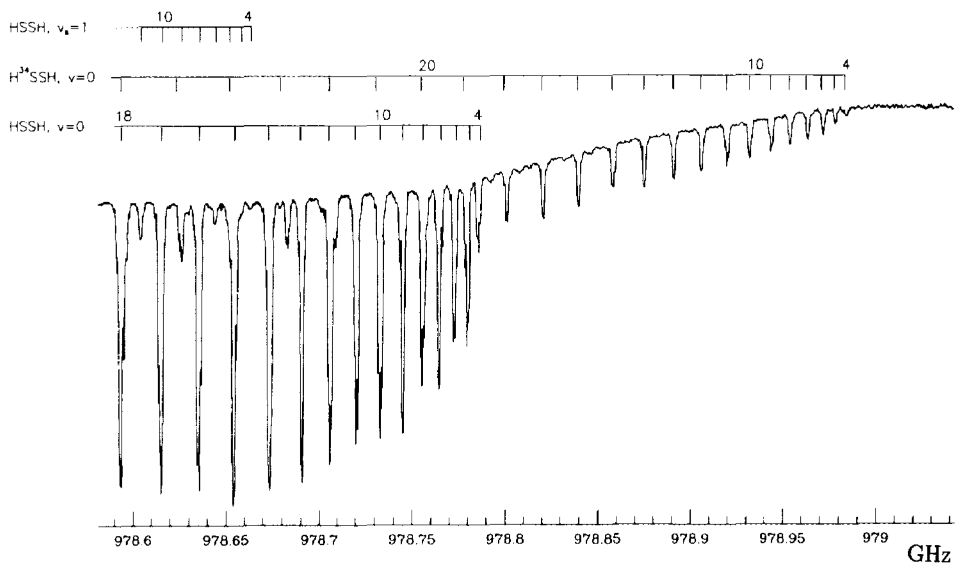

FIG. 3. Detail in the $^{r}Q_3$ bandhead. As expected from the previous analysis, the scanned bandhead region consists of a superposition of the ground state main isotopomer, HSSH, and its ^{34}S isotopomer, $HS^{34}SH$, as well as Q-branch lines of the first excited S–S stretching state.

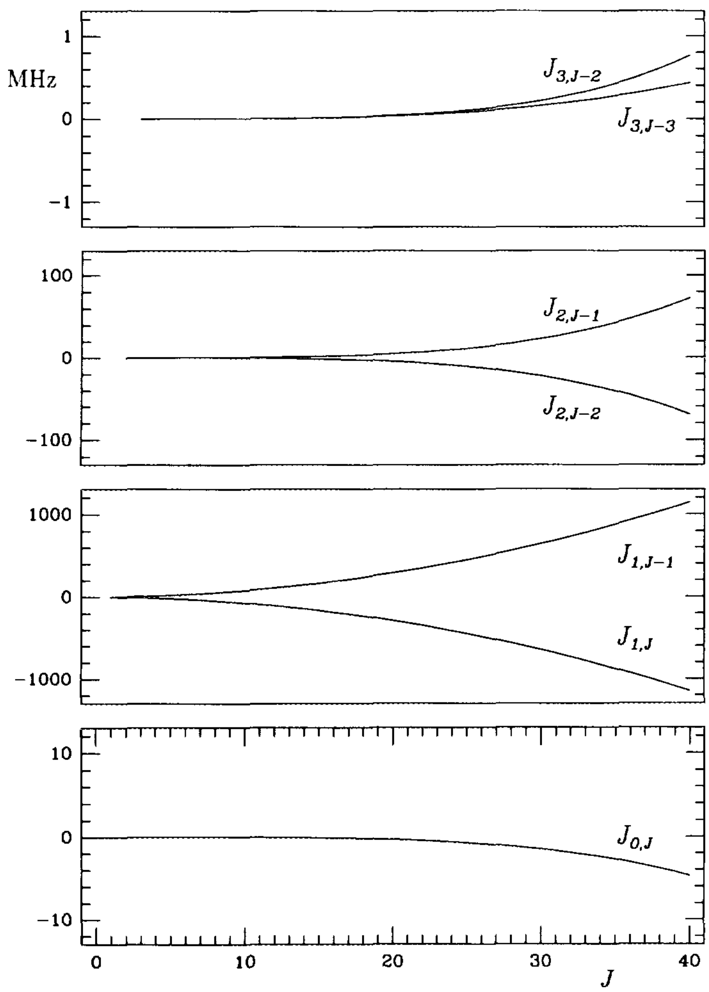

FIG. 4. The calculated K-doubling separations in HSSH are plotted as deviations from the symmetric top energy levels in MHz units for various K_a sublevels. The splittings of the K_a = 2 and 3 levels are inverted compared to the expected inertial asymmetry doubling.

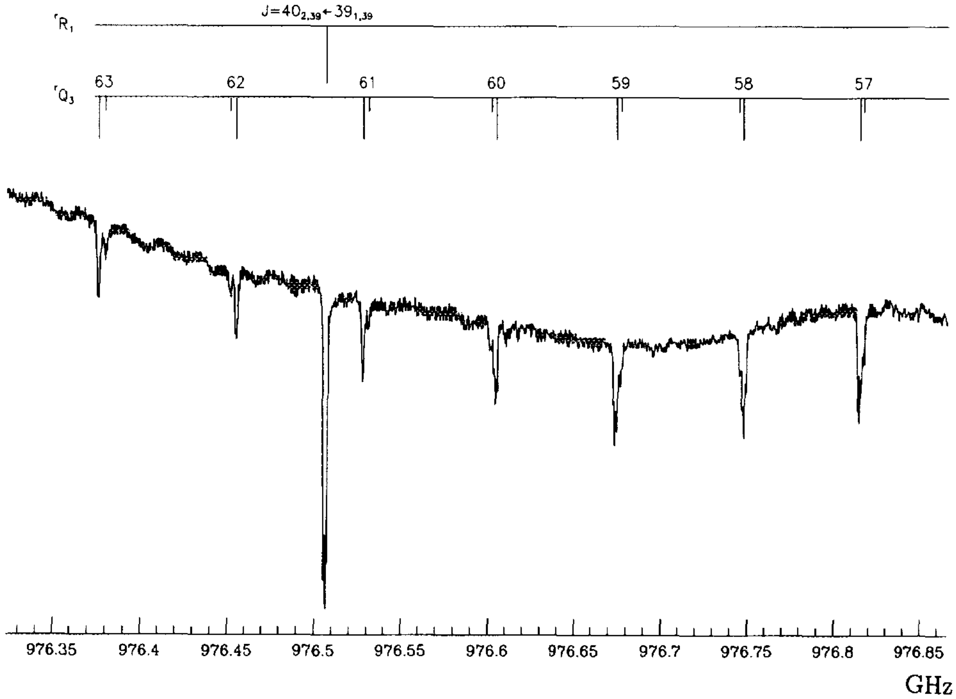

FIG. 5. The observed K-doubling in high J transitions of the $^rQ_3$ in H_2S_2. The intensities of the observed K-doublet lines are: for even J the lower frequency component carries statistical weight 1 and the upper one weight 3, and vice versa for odd J values. This intensity alternation corresponds to the anomalous K-doubling.

distortion splitting due to the matrix elements of the quartic, sextic, and higher order distortion terms in the Hamiltonian. It has been proved to be appropriate for this molecule to use Watson's S-reduced Hamiltonian,

$$\hat{H} = \tfrac{1}{2}(B + C)\hat{J}^2 + \{A - \tfrac{1}{2}(B + C)\}\hat{J}_z^2 - D_J\hat{J}^4 - D_{JK}\hat{J}^2\hat{J}_z^2 - D_K\hat{J}_z^4 + H_J\hat{J}^6 + H_{JK}\hat{J}^4\hat{J}_z^2$$
$$+ H_{KJ}\hat{J}^2\hat{J}_z^4 + H_K\hat{J}_z^6 - L_{JK}\hat{J}^4\hat{J}_z^4 - L_{KJ}\hat{J}^2\hat{J}_z^6 - L_K\hat{J}_z^8 + \tfrac{1}{4}(B - C)(\hat{J}_+^2 + \hat{J}_-^2) + d_1\hat{J}^2(\hat{J}_+^2 + \hat{J}_-^2)$$
$$+ d_2(\hat{J}_+^4 + \hat{J}_-^4) + h_1\hat{J}^4(\hat{J}_+^2 + \hat{J}_-^2) + h_2\hat{J}^2(\hat{J}_+^4 + \hat{J}_-^4) + h_3(\hat{J}_+^6 + \hat{J}_-^6). \quad (1)$$

Usually the asymmetry splitting, caused by the term with $(B - C)$, completely dominates the K-type doubling, but in HSSH and DSSD the reverse is true, namely the centrifugal distortion splitting is the more influential of the two terms, except for the $K_a = 1$ levels. In the $K_a = 2$ level the first-order perturbation due to the term with $d_2(\hat{J}_+^4 + \hat{J}_-^4)(\Delta K_a = \pm 4$ interaction) dominates for high J, and anomalous K-type doubling caused by the negative value of $d_2 = -27.3$ Hz was reported (5). For the $K_a = 3$ levels the effect of this term overrides any asymmetry effect in high J and is seen here for the first time. The dependence of the K-doubling on the quantum number J of HSSH is presented in Fig. 4 for several low K_a states, where it is seen that the order of the levels $J_{3,J-2}$ and $J_{3,J-3}$ (and of course the $J_{2,J-1}$ and $J_{2,J-2}$ levels as established earlier) is reversed from the *normal* order as given by the asymmetry splitting. This effect, which we termed anomalous K-doubling is clearly seen in all high J transitions of the $^rQ_3$ branch, whose K-doubling due to the centrifugal distortion can be resolved (Fig. 5).

For the case of the $J = 60$ transitions, the two K-doublet transitions $60_{4,57} \leftarrow 60_{3,57}$ and $60_{4,56} \leftarrow 60_{3,58}$ are observed with alternating intensity, i.e., intensity ratio 3:1 for odd K_c and even K_c (the c-principal inertial axis is the C_2 symmetry axis of HSSH) as shown in Fig. 6. The observed fact that the low-frequency component is weaker than the higher one can only be interpreted by the inverted K-doubling of the $K_a = 3$ levels. In addition, we note that the K-doubling should be *normal* for $K_a \geqslant 4$ as far as the d_2 term is considered to be the sole origin of the anomaly. The effect of $h_3(\hat{J}_+^6 + \hat{J}_-^6)$ is significant, $h_3 = -3.7$ μHz (5), but one order

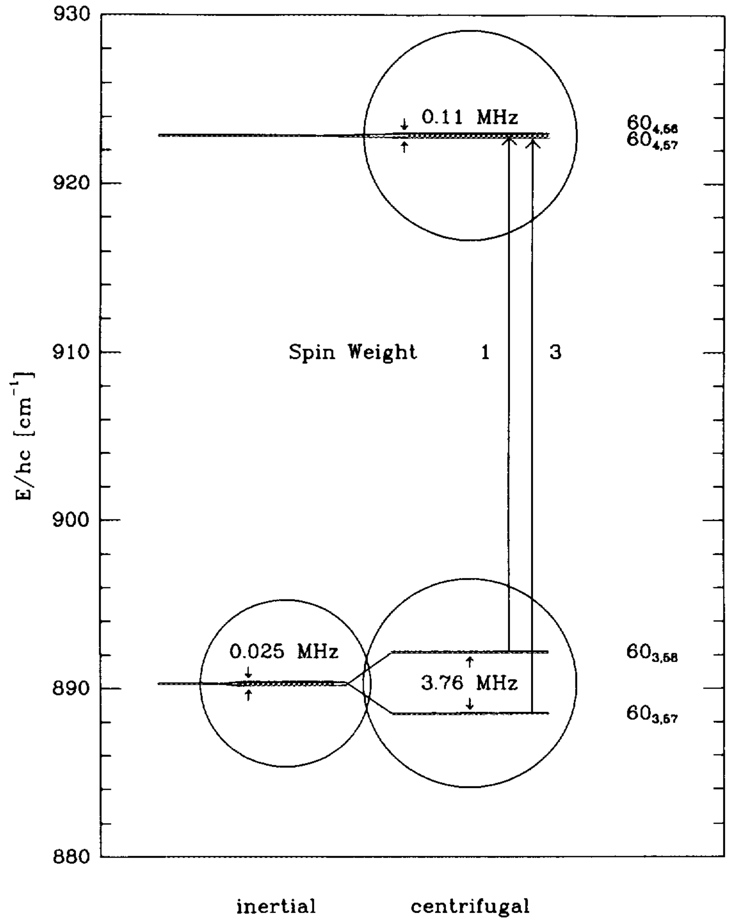

FIG. 6. Energy level diagram for two selected transitions of the $^rQ_3$ branch and contributions of the *inertial* and *centrifugal distortion* splitting terms. The inertial contribution to the K-doubling is essentially negligible. The intensity alternation due to the nuclear spin statistics indicates the anomalous K-doubling in the K_a = 3 state, the order of which is inverted by the centrifugal distortion effect.

of magnitude smaller than the d_2 contribution at $J = 60$. Finally, at the present time the radiation frequency of the source was not measured. We have calibrated the line positions using the predicted values (*5*), the accuracy of which are believed to be better than 1 MHz.

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