The $^rQ_2$-branch of HOOH at 1.05 THz

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Z. Naturforsch. **49a**, 525–529 (1994); received March 12, 1994

The lower frequency $^rQ_2$-branch of the torsional split rotational spectrum of HOOH has been recorded for the first time near 1.05 THz with Doppler limited resolution employing a Backward Wave Oscillator as the radiation source. The position of the Q-branch lines can be predicted very closely from a set of effective rotational constants derived individually for the two torsionally split levels. The symmetry of the molecule, and the height of the potential barrier against internal rotation, are the two main reasons for the clear separation between the rotational and torsional contributions to the spectrum of HOOH as well as the analogous molecule HSSH.

1. Introduction

Hydrogen peroxide, HOOH, and its sulfur analog hydrogen persulfide, HSSH, or disulfane, as it is more commonly referred to in the literature, are simple four-atomic molecules with a well known chain structure, giving both molecules a C_2 point symmetry. The two angles for both molecules, i.e. the dihedral angle, and the OOH (SSH) angle, range between about 90° and 110°. As skew chain molecules, they share a number of common general features arising from their similar structure and symmetry, and from the possibility for internal rotation of the two OH (SH) fragments relative to each other. The former similarities lead to the same coarse spectroscopic features, which are associated with perpendicular-type pure rotational spectra of slightly asymmetric rotors. The "perpendicular"-type Q-branches are highly compact, but for different K_a values widely spaced, with subband centers separated by $2\{A-(B-C)/2\}K_a$, and thus moving rapidly towards the far infrared region with increasing K_a. The lower K_a Q-branches, e.g. $K_a = 1-0$, $2-1$, have been studied with microwave techniques, which have until recently been limited to frequencies below ~ 1 THz, see e.g. [1–3]. Above 40 cm^{-1}, the Q-branches of both molecules have been recorded by Fourier transform spectroscopy [4, 5].

2. Spectral Features – Torsional Effects

Despite their general similarity, the measured rotational spectra of HOOH and HSSH display a rather different appearance, mainly due to differing barrier heights towards internal rotation. Whereas the cis barriers of HOOH and HSSH are rather similar (V_{cis}(HOOH) = 2460 cm^{-1}; V_{cis}(HSSH) = 2843 cm^{-1}), the trans barriers differ rather substantially (V_{trans}(HOOH) = 385 cm^{-1}; V_{trans}(HSSH) = 2037 cm^{-1}) from each other [4, 6, 7]. The faster tunneling through the trans-barrier in HOOH has a significant effect on the rotational spectrum of HOOH and is most clearly seen in the two symmetrically shifted positions of the torsionally split $^rQ_{K_a}$-branches relative to the high barrier case. In particular, the low trans-barrier of HOOH produces a 686 GHz splitting in the ground state rotational transitions, whereas for HSSH this splittig is only 150 kHz and can essentially be neglected in Doppler-limited spectroscopy.

The effect of the torsional splitting in HOOH is most clearly displayed in a plot of the subband centers of the $^rQ_{K_a}$-branch vs. the K_a quantum number, as shown in Figure 1. For HSSH, where the torsional splitting is negligible small and is therefore not recognizable in this type of plot, the subband center positions in dependence of the quantum number K_a follow

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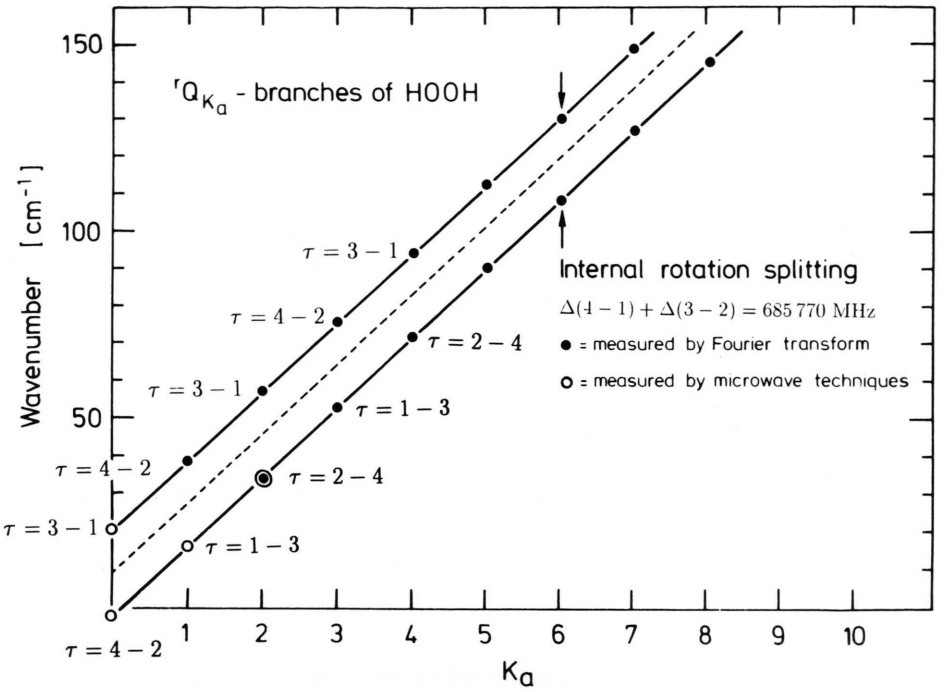

Fig. 1. Positions of the K_a-subband centers in wavenumber for the torsional ground state of HOOH. The dashed center-line marks the origin of the hypothetically unsplit band centers. However, due to torsional tunneling each sub-band center is doubled, leading to the two parallel drawn-out lines with their respective positions marked by a dots. For each K_a-value, the appropriate transitions are identified by the additional quantum number $\tau = 1, 2, 3, 4$, which is required to specify the four torsional energy levels.

essentially a single, straight line with a slope determined by the almost constant spacing of the Q-branches. For HOOH, on the other hand, the situation is rather different. Here the position of each K_a-subband center is shifted relative to its unsplit origin by a ± 343 GHz separation of the torsional energy levels. Thus for HOOH the torsional splitting leads to the two approximately parallel straight lines shown in Fig. 1, resulting in an upper and a lower Q-branch series relative to the hypothetical unsplit positions. Thus a fairly complex sequence of Q-branch positions vs. frequency emerges.

The complexity of the resulting HOOH spectrum is especially enhanced because the torsional splitting is comparable with the hypothetical Q-branch spacing expected for the low-barrier case. In fact, the large torsional splitting leads for the lower of the two torsional-split $^rQ_0$-branches to the peculiarity that the $K_a = 1$, $\tau = 2$ torsionally-split levels lie energetically lower than the $K_a = 0$, $\tau = 4$ level. In Fig. 2 we compare the three lowest K_a torsional-rotational levels of HSSH with those of HOOH in the vibrational (and torsional) ground state. For HSSH, the order in the rotational K_a energy level structure is regular and little affected by the torsional splitting. Consequently, the normal, well-known c-type spectrum results, which for the lowest torsional state reveals the influence of the torsional splitting only under sub-Doppler resolution [8]. For HOOH, on the other hand, the reversal of the energy levels for the $^rQ_0$-branch ($\tau = 4-2$) leads to the apparent appearance of a b-type spectrum, i.e. the frequency increases with increasing J quantum number, although the c-axis remains aligned to the C_2-symmetry axis.

3. $^rQ_2$-branch

The spacing of the different J lines within a given Q-branch is determined by the combined effects of inertial asymmetry and centrifugal distortion of the molecule. In addition, for HOOH, effects due to the interaction between rotation and internal rotation cannot be neglected entirely, even not for the ground

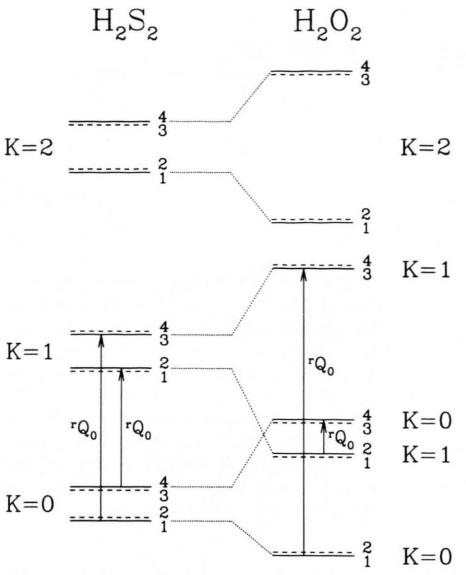

Fig. 2. Schematical comparison between the ground state torsional-rotational energy levels of HSSH and HOOH for low K_a values. The energy levels are not drawn to scale. For HOOH the large torsional splitting leads to the peculiarity that the $K_a = 1$, $\tau = 2$ level lies below the $K_a = 0$, $\tau = 4$ level. The levels indicated by broken lines are not existing. The pure rotational transitions for the $^rQ_0$-branches of HSSH and HOOH are indicated. Note that the torsional splitting for HSSH is only 150 kHz, whereas for HOOH it is 686 GHz.

state spectrum. Since both molecules are very close to accidental symmetric tops, with asymmetry parameters $\varkappa$(HOOH) = −0.99 and $\varkappa$(HSSH) = −0.99996, their Q-branches are very compact, especially for the case of HSSH. Its high intensity makes the Q-branch pattern easily discernible and furnishes the outstanding characteristic of the pure rotational spectrum.

In Fig. 3 we present for the first time in Doppler-limited resolution, the recording of the $^rQ_2$-branch of HOOH at 1.038 THz, using a backward wave oscillator (BWO), made by ISTOK – Research and Production Corporation, based near Moscow. With the exception of the tube itself, the experimental techniques used are the same as reported for the observation of the $^rQ_3$-branch of HSSH at 980 GHz [9]. It may just be mentioned here that the BWO has been operated in the free running mode, and as such absolute frequency measurements could not be performed. The recorded spectra, however, serve as a typical example of the BWO's fine tuning capabilities. Very recently we have succeeded in frequency- and phase-stability the BWOs into the Terahertz-region.

We have depicted in Fig. 3 the region close to the band center, where the position of the low J lines still forms a fairly easily recognizable pattern with the typ-

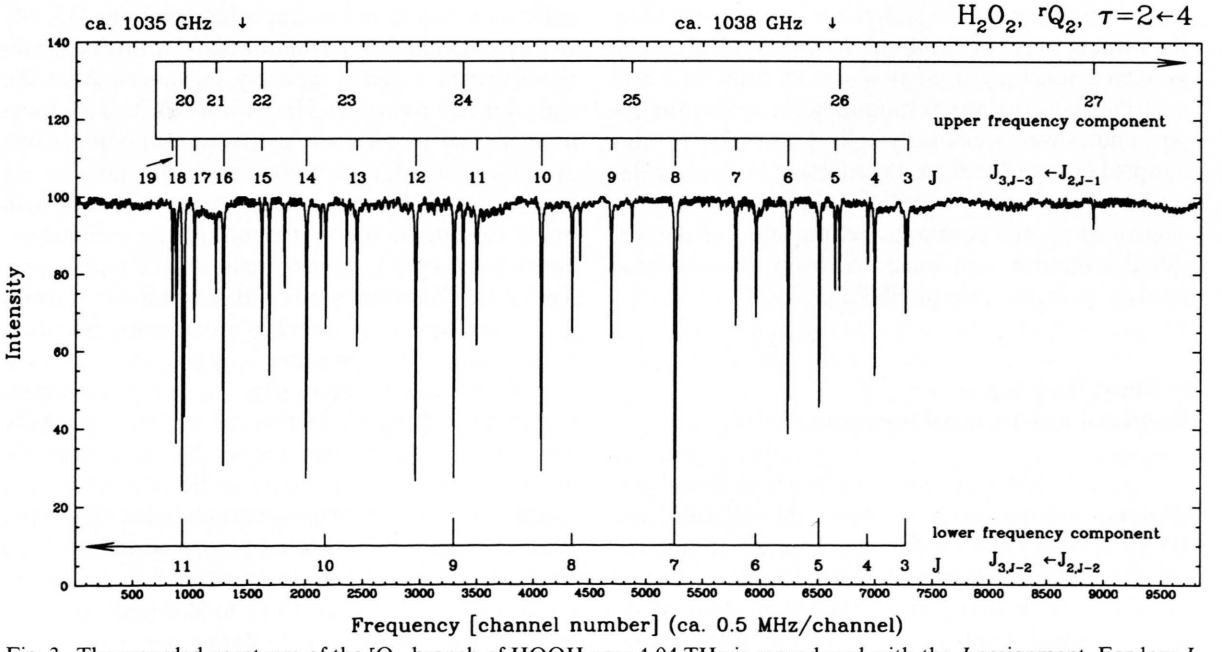

Fig. 3. The recorded spectrum of the $^rQ_2$-branch of HOOH near 1.04 THz is reproduced with the J-assignment. For low J values the asymmetry splitting is small enough to result in an easily recognizable line pattern of the band head, the assignment of which is helped by the characteristic nuclear spin 1:3 intensity alternation of the hydrogen nuclei starting with $J = 3$.

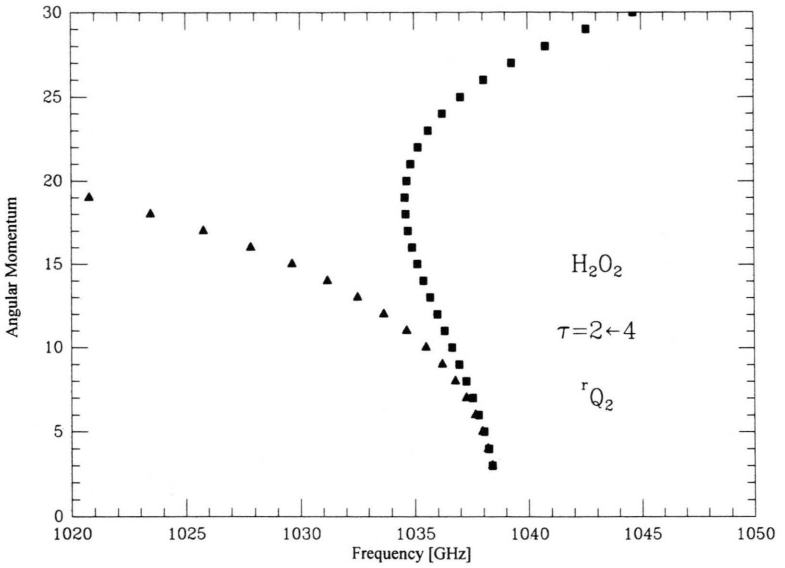

Fig. 4. FORTRAT diagram of the predicted $^rQ_2$-branch of HOOH. The inertal asymmetry causes a splitting into two branches, which for low and medium J values overlap. The predicted turning point of the upper K-split branch occur between $J = 19$ and 20 as observed. For J values lower than 19, the upper K-branch starts off towards lower frequencies and leads to the observed overlap region.

ical alternating nuclear statistical weights of 3:1, associated with the two hydrogen nuclei with nuclear spin $I = 1/2$. It might be noticed that the inertial asymmetry doubling (K-type doublets) produces for the lowest J-transition a detectable splitting, which increases rapidly with increasing J quantum numbers and leads to the Fortran diagram displayed in Figure 4. The relative position of the individual J-lines, including the turning point of the upper K-split branch, can be predicted precisely from two sets of rotational and centrifugal distortion constants determined for the upper and lower torsionally-split levels [2]. In this adopted fitting procedure, the effects of torsional-rotational interaction are completely absorbed in the set of effetive rotational constants, i.e. the effect of the torsional motion is well separated from the rotational motion, as in the case of HSSH.

4. Theoretical Aspects – Rotational and Torsional Separation

It is of interest to ask why the rotational and torsional contributions to both the HOOH and HSSH spectra are so separable. After all, in internal rotor molecules such as methanol, methylformate, and acetaldehyde, there is a strong torsional-rotational interaction which complicates the rotational spectra, especially for K-changing transitions [10–12]. In this section we use simply K in place of K_a. There are two reasons for the lack of rotational-torsional interactions in HOOH and HSSH, briefly discussed by Hunt et al. [13]. First, and of lesser importance, it is the symmetry of the molecules. In the internal axis method (IAM) treatment of internal rotation, the axes used are defined so that internal rotation consists of the two parts of the molecule rotating with equal angular momentum but in opposite directions [13, 14]. In this axis system, the Hamiltonian for torsional motion appears to be completely decoupled from the end-over-end rotational Hamiltonian. The basis functions needed to solve the eigenvalue equation, however, must, in addition to free rotor functions of the type $\exp(i m \gamma)$, contain a factor $\exp(i \varrho K \gamma)$ to remain single valued. In the arguments of the exponential functions, γ is the torsional angle, m an integer representing the quantum number for a free internal rotor, K the end-over-end angular momentum quantum number along the symmetry axis (i.e., the a-axis for HOOH and HSSH), and ϱ ($0 \leqq \varrho \leqq 1$) a unitless measure of the fraction of the moment of inertia along the molecular symmetry axis due to that portion of the molecule (the "top") assumed to be undergoing the actual motion before transformation to the IAM axes. With this basis, the diagonal matrix elements of the torsional Hamiltonian matrix are found to depend on the expression $(m + \varrho K)$, which indeed leads to a coupling between end-over-end rotation and torsion. For methyl formate ($\varrho = 0.085$), acetaldehyde ($\varrho = 0.329$) and methanol ($\varrho = 0.810$), where the quoted ϱ values

derive from treatments in which the methyl group is considered to be the top, the torsional energy levels resulting from the matrix diagonalization have a non-symmetric dependence on K. Thus, rotational transitions with $\Delta K \neq 0$ can be affected in a non-trivial manner. But, for HOOH and HSSH, ϱ is exactly 1/2, so that the dependence reduces to a distinction only between even and odd values of K. For even K, the product ϱK is an integer, and the torsional eigenfunctions (characterized by $\tau = 1, 4$ or by the permutation-inversion group designations A_{1s}, A_{2s}) can be expressed as sums of trigonometric or imaginary exponential functions with arguments $n'\gamma$, where $n' = m + \varrho K$ is an integer [6, 13]. For odd K, the product ϱK is a half-integer and the torsional eigenfunctions (characterized by $\tau = 2, 3$ or by the permutation-inversion group designations A_{2d}, A_{1d}) can be expressed as sums of trigonometric or imaginary exponential functions with arguments $n'\gamma$, where $n' = m + \varrho K$ is a half integer. Even if noticeable, rotational-torsional coupling can only serve to cause an alternation in energy between rotational-torsional energy levels with even and odd K. Given the $\Delta K = \pm 1$, $\tau = 1 \leftrightarrow 3, 4 \leftrightarrow 2$ selection rules, moreover, pure rotational transitions cannot even distinguish this alternation [6].

If the above explanation were the only reason that strong torsional-rotational interaction is not apparent in the spectra of HOOH and HSSH, then it could be argued that the spectra of HOOD and HSSD should show strong interaction, since for these spectra ϱ is not exactly 1/2. However, there is a second reason, and that is the height of the potential barrier against internal rotation. Although their trans barriers are different, HOOH and HSSH share a large cis barrier against internal rotation. For torsional levels considerably under this barrier, the internal motion is characterized more as a large amplitude vibration than as internal rotation. As the torsional energy increases, the internal rotation character of the motion becomes more apparent. For HOOH and HSSH this will lead only to a distinction between the torsional splitting involving rotational-torsional levels of odd K ($\tau = 2, 3$) and even K ($\tau = 1, 4$), as has already been detected in FIR spectral transitions [4, 6]. For HOOD and HSSD, the analogous rotational-torsional interaction will be more complex in character, especially for HOOD.

Acknowledgements

We are especially grateful to Professor Frank De Lucia for providing us with the predicted frequencies of the HOOH lines observed here. We thank the Deutsche Forschungsgemeinschaft for support of this work via Special Research Grant SFB-301, including the stay of E. H. The work of A.F.K. and S.P.B. at Cologne was made possible by the DFG through grants aimed to support Eastern and Central European countries and the Republics of the former Soviet Union. A.F.K. thanks the German Embassy in Moscow for issuing an entrance visa to Germany in proper time, so this experiment could be carried out.

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