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Introduction

HSOH, either known as oxdisulfane or hydrogen thio-peroxide, can be considered a “link molecule” in between the molecules HSSH, disulfane, and HOOH, hydrogen peroxide (see Figure 1.1). The chemical and structural properties of the brethren molecules HSSH and HOOH are well known to chemists for many decades[1]. On the contrary only little information is available for HSOH.

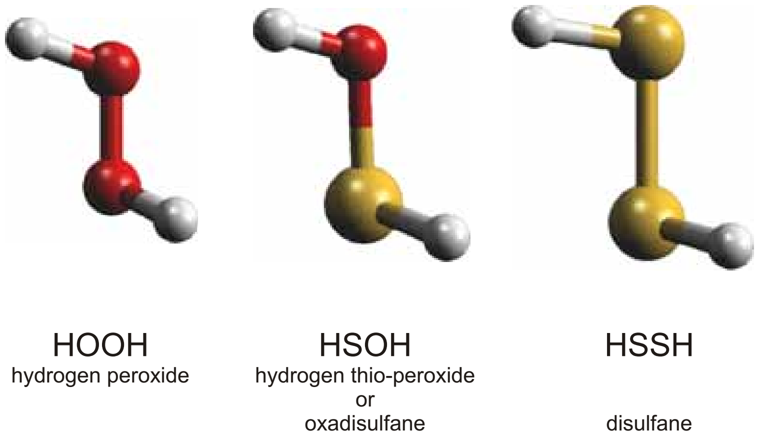

Figure 1.1: The kin molecules HOOH, HSOH, and HSSH.

Experimental data on gas-phase HSOH were hampered by the difficulties of its synthesis for a long time and became available only recently [123]. Smardzewski and Lin recorded infrared spectra of products from photolysis of ozone (O_3) and hydrogen sulfide (H_2S) trapped in an argon matrix and they assigned some of the spectral features to vibrational modes of HSOH [105]. Later on, Iraqi and Schwarz detected HSOH via mass spectroscopy

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[1] See for HOOH: [46, 95, 96, 107] and for HSSH: [11, 16, 40, 47, 121].

in a chemical ionization source from a H_2S/N_2O gas mixture [64]. However, none of these syntheses were suited for gas-phase detection of HSOH by means of absorption spectroscopy. Winnewisser, Hahn, and co-workers began to hunt down HSOH and it took them at least 15 years of trial and error before the breakthrough came in 2003. Behnke and Hahn [10, 123] found a novel method of producing oxadisulfane in large quantities from flash vacuum pyrolysis of di-*tert*-butyl sulfoxide. The chemical reaction creating HSOH additionally builds many other similar molecules simultaneously. Given those circumstances, synthesizing HSOH and recording its spectrum in the laboratory was not so much like "searching for a needle in a haystack" but rather like "looking for an ant somewhere in Canada", Behnke said. Nevertheless, this synthesis enables measurements of the rotational spectra of HSOH, and due to extremely precise prognoses based on high level quantum chemical *ab initio* calculations by Gauss *et al.*, Winnewisser *et al.* [123] succeeded in assigning the rotational spectrum of this elusive species.

The molecule HSOH is an asymmetric rotor close to the limiting case of a symmetric prolate top molecule. Therefore the pure rotational and rotational-vibrational spectra of this molecule appear very simple at first glance. However, if the spectra are inspected in detail, the molecule manifests its peculiarities which require the reexamination of some of the basic concepts in vibration-rotation theory.

HSOH, as well as HSSH and HOOH, is one of the most simple examples for a molecule showing chirality. In Figure 1.2 the two stable configurations are shown, they are energetically but not geometrically identical. This means that they are not congruent. One configuration forms the so called right-handed and the other the left-handed isomer. However, the two isomers cannot be separated. They change their configuration forth and back between right-handed and left-handed by tunneling through the potential

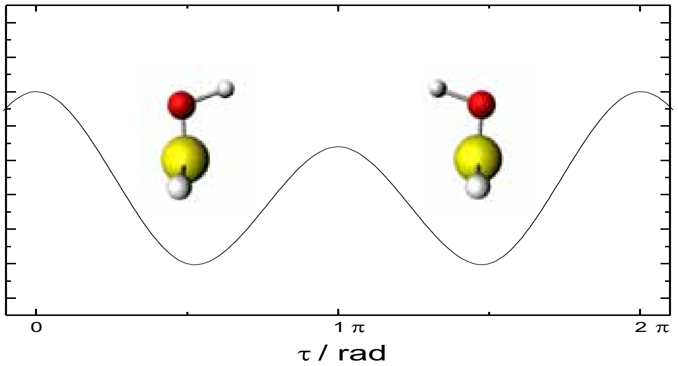

Figure 1.2: The enantiomers of HSOH.

barrier separating the enantiomers[2].
The tunneling process through the barrier is an internal rotation about the S-O bond in HSOH. Obviously, HSOH is of lower symmetry than HSSH and HOOH. Hence HSOH is not only one of the simplest examples of a molecule showing chirality but with two different rotor moieties, SH and OH, it also represents the most general case of an internally rotating four atomic chain molecule. The recorded transitions of HSOH split into doublets due to the internal rotation tunneling. In order to give an explanation of the observed line splitting it is necessary to extend the period of internal rotation from 2π to 6π, meaning HSOH has not only one left and one right handed isomer but rather six enantiomers.

Furthermore, in the HSOH spectra presented here another new effect of fundamental spectroscopic importance has been observed: The spectra of HSOH exhibit an intensity anomaly. This effect is most probably related to a state-mixing and should be observable in case of all asymmetric top molecules bearing a hindered internal motion and having at least two different dipole moment components. Even though this effect seems to be of general nature it has not been reported so far.

The high frequency stretching modes ν(SH) and ν(OH) exhibit entirely different traits of the molecule HSOH. In case of the OH-stretching mode the molecule can be regarded as a fairly rigid “textbook” molecule, displaying unperturbed spectra. On the contrary, the spectra observed in case of the SH stretching mode display a strong potential coupling and hence, identify the limits given by the model of normal modes.

HSOH is not only interesting because of its fundamental spectroscopic importance but it attracts the attention of chemists as well.
Sulfur forms a large number of oxoacids, $H_xS_yO_z$. Sulfur oxoacids are widely considered to occur in the formation of pollutants in the Earth’s upper atmosphere [29, 113, 108, 91] and combustion chemistry of sulfur [42]. Most of these compounds are too unstable to be isolated in pure form. Consequently, the physical and chemical properties of these important species are not well-known. The most simple (’mononuclear’) oxoacids of sulfur are of composition H_2SO_n with n ranging from 1 to 4. For none of these species an experimental equilibrium structure in the gas-phase has been reported, yet. HSOH is the smallest member of oxygen counting sulfur acids and it is the basic molecule exhibiting a S-O single bond. The S-O bond in molecules such as HSO, SO, or SO_2 is known to possess multibond character. Up to date no experimental value for a S-O single bond has been reported.
In addition to its role in atmospheric chemistry, there is some evidence, that HSOH is formed in the interstellar medium [33, 34], too.

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[2] That means: mirror images.

The most powerful tool to investigate the structure as well as the dynamics of a molecule is given by means of spectroscopy.
Molecular spectroscopy involves the study of the absorption and emission of electromagnetic radiation by matter; the radiation can be detected directly, or indirectly by its effects on certain molecular properties. The primary purpose of spectroscopic studies is to understand the nature of the nuclear and electronic motions within a molecule.
The different branches of spectroscopy may be classified either in terms of the wavelength, or frequency, of the electromagnetic radiation, or in terms of the type of intramolecular dynamic motion involved as shown in Figure 1.3.

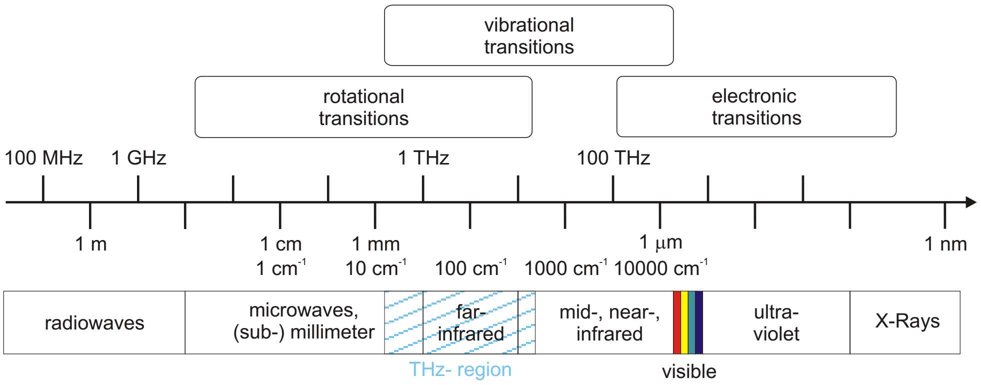

Figure 1.3: Schematic diagram of the electromagnetic spectrum and corresponding interactions of radiation with molecules.

Molecular spectroscopy covers a nominal energy range from 0.0001 cm^{-1} to 100000 cm^{-1}, nine decades in energy, frequency or wavelength. The experimental techniques employed over the full range given in Figure 1.3 are multifarious. In the experimental part of this thesis, spectra in the submillimeterwave, THz, and mid-IR region have been recorded by employing quite different experimental setups. Details on the spectrometers introduced are given in Chapter 4 of this thesis.
Molecular spectra arise from electronic, vibrational, and rotational transitions. These motions are not independent from each other, and the complexity of the spectra is increased by the possibility of interactions between them. If they can be analyzed, the information they yield should be correspondingly valuable, it is possible to extract details of molecular dimensions, the strengths of bonds, and the shapes of molecular potential energy curves. The energy associated with rotational transitions is usually lower than that involved in vibrational transitions, which in turn is usually lower than in electronic transitions. As a consequence, although it is possible to observe pure rotational spectra (in the *microwave* region) a vibrational motion is generally accompanied by rotational transitions. A vibrational spectrum (in the *infrared* region) is thus superimposed by a structure due to simultaneous rotational transitions. In an electromagnetic transition both vibrational and

rotational transitions are stimulated and the spectrum (in the *visible* and *ultraviolet* regions) contains information on all of them.

The outline of the present thesis is as follows: The fundamental theoretical concepts related to rotational and vibrational spectroscopy of molecules, as well as introductory information on deriving molecular structures are given in Chapter 2.
This thesis is an example for the fruitful interplay of theoretical and experimental studies and hence, a brief overview on quantum chemical calculations is presented in Chapter 3.
The study of transient molecules requires spectroscopic methods high in sensitivity, resolution, versatility, et cetera. Thus, steady effort is necessary to develop new techniques and to improve existing instruments. In Chapter 4 information on the various experimental setups and spectrometers employed in the experimental part of this thesis are presented.
Chapter 5 deals with the different ways to synthesize the transient species HSOH under laboratory conditions. Besides the well established method of synthesizing the molecule via pyrolysis of di-*tert*-butyl sulfoxide a new production method for the molecule in a *rf*-discharge of water and pure sulfur has been examined. Furthermore, a brief discussion on the possibility of HSOH production in the interstellar medium is given in this chapter as well.
The first gas-phase detection of the singly-deuterated oxadisulfane HSOD is presented in Chapter 6. The results of these measurements on HSOD were substantial for the evaluation of an experimental equilibrium structure of HSOH, in Chapter 7.
To get information not only on the structure of this elusive species, but also its dynamics the studies have been extended to the infrared region. The vibrational-rotational spectra recorded in course of this thesis are analyzed in Chapter 8.
Before concluding remarks and prospects are given in Chapter 10, Chapter 9 deals with the subject of internal dynamics in HSOH. New experimental results have been obtained by measurements in the THz-region. These findings identified the limits of theory available at that time and triggered intense theoretical studies on the internal rotation tunneling in this molecule. Furthermore Chapter 9 presents a new, so far unknown, fundamental characteristic of asymmetric top molecules, that possess a barrier to internal rotation tunneling.