

Abstract

In the course of this thesis, two different molecular species have been studied. Both are connected to different aspects of rotational spectroscopy regarding the challenges in the investigation as well as the scientific questions. Oxatrisulfane (HSSOH) is a molecule of chemical interest with the focus on obtaining the geometric structure and the stability of possible configurations of oxasulfanes. Since it is a very reactive molecular species, which is not stable even under laboratory conditions, the production of oxatrisulfane is the bottleneck to a spectroscopic investigation. Königshofen *et al.*¹ synthesized HSSOH via flash vacuum pyrolysis of the precursor molecule *tert*-butylthiosulfinic acid *S-tert*-butylester. In the work presented here, the pyrolysis conditions have been investigated in detail to optimize the synthesis of oxatrisulfane. Among a large number of additional byproducts, two conformeric structures of 1-oxatrisulfane, *trans*- and *cis*-HSSOH, have been unequivocally identified by their rotational spectrum for the first time. The detailed analysis of the rotational spectrum given in this thesis yields spectroscopic parameters that are in excellent agreement with the results of latest high-level *ab initio* calculations. The *trans* conformer was found to be slightly more stable than the *cis* configuration of 1-oxatrisulfane.

The second molecular species investigated in the course of this thesis, the ¹³C-isotopologues of dimethyl ether (¹³CH₃O¹²CH₃ and (¹³CH₃)₂O), are stable molecules, but the analysis of their rotational spectrum is challenging due to large amplitude motions of the two methyl groups. The development of spectroscopic models for molecules undergoing internal rotation is still ongoing, involving combined theoretical and experimental efforts. In the course of this thesis, rotational-torsional transitions within the vibrational ground state have been recorded for both ¹³C-isotopologues of dimethyl ether, covering a broad spectral region from millimeter to sub-mm wavelengths. Employing the Effective Rotational HAMILtonian **ERHAM** by P. Groner, the spectra of both isotopologues have been reproduced within their experimental uncertainties. A second theoretical model, **BELGI-Cs2tops**, which has only recently been developed by I. Kleiner *et al.*, has been tested to analyze the ground-state spectrum of ¹³CH₃O¹²CH₃. Due to the large barriers to torsion in dimethyl ether, this analysis suffers from strong correlation of the spectroscopic parameters in this model. Significant improvement is expected, when torsional excited states are included in the analysis.

In addition, isotopologues of dimethyl ether are of strong astronomical interest. The identification of new complex molecules in the interstellar medium is hampered by the huge number of spectral features in molecular line surveys. However, a large fraction of the observed transitions belongs to a limited number of prominent molecules like dimethyl ether, which show strong and dense spectra and thus cover the spectral features of other molecules. Therefore, also precise predictions for the spectrum of isotopologues of these prominent species are essential to overcome the line confusion, and to enable the detection of more exotic species in the interstellar medium.

Furthermore, the relative isotopic abundance ratios of molecular species in the interstellar medium can contain information on their formation processes. These ratios are important pieces in the big puzzle of astrochemical networks which aim towards the understanding of the evolution of star-forming regions.

Based on the analysis performed with **ERHAM**, accurate predictions of transition frequencies and intensities for the vibrational ground state of ¹³CH₃O¹²CH₃ and (¹³CH₃)₂O

¹Königshofen *et al.* *Z. Anorg. Allg. Chem.* **625**, 1779–1786 (1999)

have been provided for astronomical application. These data are an important contribution for future astronomical observations performed with the latest generation of instruments like the Atacama Large Millimeter Array (ALMA). The predictions already led to the first interstellar detection of $^{13}\text{CH}_3\text{O}^{12}\text{CH}_3$ in a survey of the star-forming region G327.3–0.6 performed with the Atacama Pathfinder Experiment (APEX).