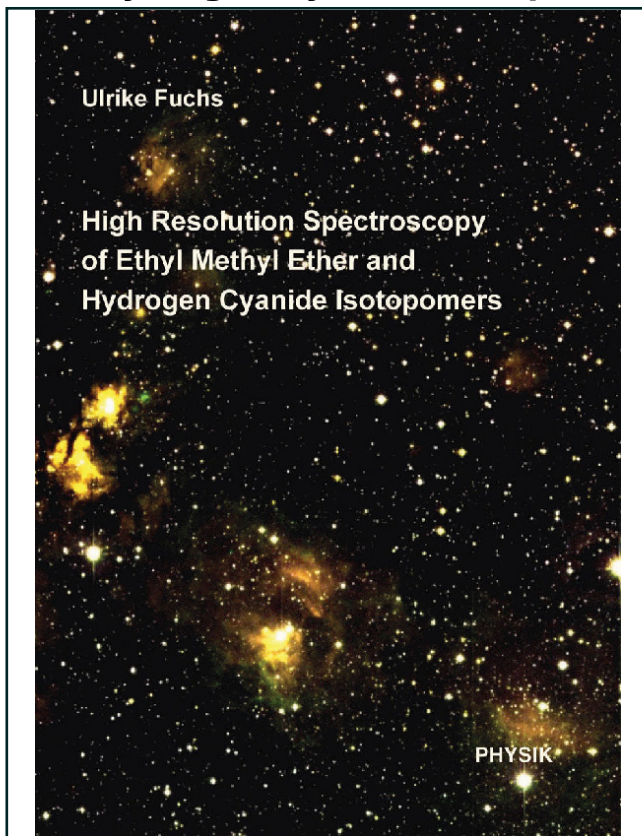




Ulrike Fuchs (Autor)

## **High Resolution Spectroscopy of Ethyl Methyl Ether and Hydrogen Cyanide Isotopomers**



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# 1. Introduction

Laboratory spectroscopy in the mm- up to the IR-region is the most extensive tool to determine structure and characteristic properties of molecules. Within this region, the rotational and vibrational motions of molecules can be studied in very detail. This work presents rotational spectra in the THz-region, obtained with backward wave oscillators (BWOs) as radiation sources which enable high resolution measurements from 120 up to 1225 GHz [Winnewisser, 1995].

The combination of laboratory studies, theoretical astronomical modeling, as well as astronomical observations is necessary in order to understand the organic chemistry of dense interstellar molecular clouds. For identification and kinematical analysis of molecular species, knowledge of accurate laboratory frequencies is inevitable. To date more than 130 molecules are identified in the interstellar medium, indicating a rich and diversified chemistry. Molecules with more than three atoms are predominantly found in high density cores [Winnewisser and Kramer, 1999] which are often regions of active star formation, like e.g. Orion [Caselli et al., 1993]. Since dimethyl ether has already been observed in this region [Snyder et al., 1974], detection of the more complex ethyl methyl ether might also be feasible. Because of the assumed reaction process leading to ethyl methyl ether, [Charnley et al., 1995] stated that a detection of this molecule is important for the oxygen-rich chemistry in hot cores. In contrast to ethyl methyl ether, low rotational transitions of hydrogen cyanide (HCN) and its mono-substituted isotopes ( $\text{H}^{13}\text{CN}$ ,  $\text{HC}^{15}\text{N}$ , and  $\text{DCN}$ ) are already known in interstellar space. HCN plays a key role in nitrogen-rich chemistry in hot cores due to its high abundance [Boonman et al., 2001].

## Ethyl methyl ether ( $\text{CH}_3\text{CH}_2\text{OCH}_3$ )

Up to now, only few laboratory data have been recorded for the complex molecule ethyl methyl ether (see figure 1.1). For ethyl methyl ether, two conformers (*trans* and *gauche*) exist which are separated by potential barriers (see in more detail [Durig et al., 2002]). The *trans*-isomer corresponds to the minimum energy level and the rotational-torsional spectrum of this conformer has been studied in laboratory with microwave spectroscopy. However, published laboratory measurements of *trans*-ethyl methyl ether extend only up to 34 GHz [Hayashi and Kuwada, 1975]. Therefore, further research extending these data to higher frequencies had been necessary. Therefore, the objective of this thesis is to present new laboratory measurements, as well as assignments and predictions for the rotational-torsional spectrum of ethyl methyl ether in its vibrational-torsional ground state up to 400 GHz in frequency. Since ethyl methyl ether is an asymmetric top molecule with two

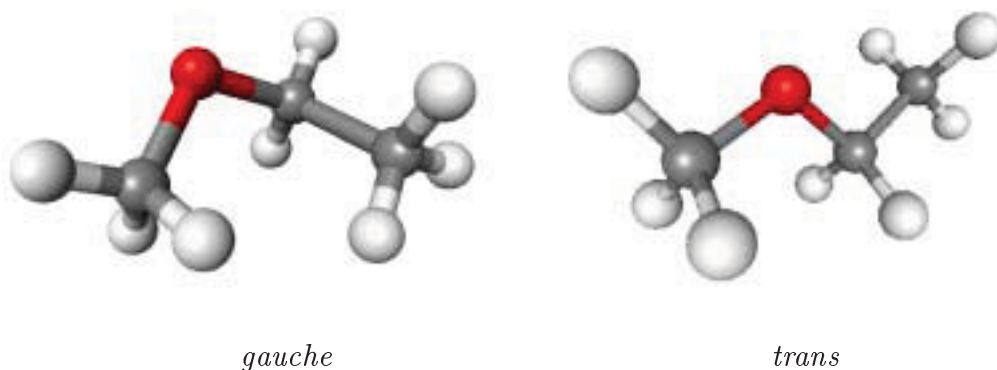


Figure 1.1.: Molecular structure of ethyl methyl ether in the two different isomers: *gauche*-ethyl methyl ether (left) and *trans*-ethyl methyl ether (right)

internal rotors consisting of its two methyl groups, this molecule is very difficult to describe. Within this context, internal rotation refers to the motion of the methyl groups (CH<sub>3</sub>) relative to the bonding axes which is defined by the carbon atoms of the methyl groups and the nearest heavy atoms (O and C), respectively. A further complication arises due to rotation of the two internal rotors against slightly different barriers. This situation causes the splitting of each rotational line into multiplets of up to five lines. For analysis, a fit routine from [Groner, 1997] is applied based on an effective rotational Hamiltonian for two periodic large-amplitude motions. However, this Hamiltonian had to be expanded to perform calculations referring to molecules with nonequivalent internal rotors [Fuchs et al., 2003]. With this, it is now possible to handle two different internal rotors in an asymmetric top molecule as well as the more common situation of two equivalent internal rotors. Moreover, it can be used to determine the spectroscopic parameters by applying the weighted nonlinear least-squares method and to predict transition frequencies as well as line strengths. Asymmetric molecules like ethyl methyl ether reveal fairly dense rotational spectra. For examination of such molecules it is advantageous to gain a broad overview spectrum which at the same time provides detailed spectral information. To serve this purpose, measurements have been performed using the FASSST spectrometer which allows fast scans (10 GHz/s) over a wide spectral range [Albert et al., 1998]. Complementary to that, transitions with small (internal rotation) splittings can be resolved using the Cologne THz spectrometer.

It is likely that ethyl methyl ether (C<sub>2</sub>H<sub>5</sub>OCH<sub>3</sub>) can be observed in interstellar space [Charnley et al., 1995] since the less complex dimethyl ether (CH<sub>3</sub>OCH<sub>3</sub>) has already been detected in hot cores within dense interstellar clouds [Charnley et al., 1992]. A tentative detection of ethyl methyl ether towards SgrB2(N), W51 e1/e2, and Orion-KL has earlier been claimed by [Charnley et al., 2001]. During the process of high-mass star formation temperatures of 100 - 300 K are reached in these hot cores, resulting in the evaporation of ice mantles from interstellar dust grains. The mantles are assumed to contain alcohol ices such as methanol (CH<sub>3</sub>OH) and ethanol (C<sub>2</sub>H<sub>5</sub>OH) [Herbst, 2001]. During the evaporation process of the mantles, alcohols

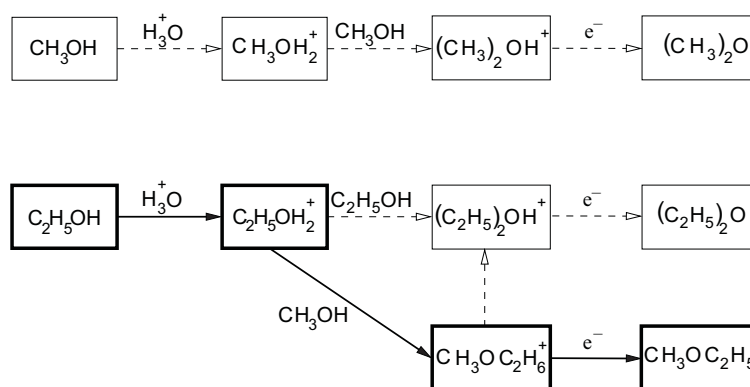


Figure 1.2.: “Schematic of the principal ion-molecule reaction paths leading from methanol and ethanol to ethers.” (taken from [Charnley et al., 1995] p. 233)

are partially converted into ethers by ion-molecule reactions between protonated alcohols (e.g.  $\text{CH}_3\text{OH}_2^+$ ) and alcohols (e.g.  $\text{CH}_3\text{OH}$ ). For dimethyl ether ( $\text{CH}_3\text{OCH}_3$ ) as simplest ether form this process is illustrated in figure 1.2. Regarding ethyl methyl ether, this reaction takes place between protonated ethanol ( $\text{C}_2\text{H}_5\text{OH}_2^+$ ) and methanol ( $\text{CH}_3\text{OH}$ ). The model of [Charnley et al., 1995] predicts that a fractional abundance with respect to molecular hydrogen of  $\sim 10^{-8}$  can be produced within  $10^4$  years after the beginning of the evaporation process of the grain mantles. Such a fractional abundance should be easily detectable with an appropriate data set of ethyl methyl ether. Thus, the presented data set should enable an extensive search for the astrophysically undetected ethyl methyl ether in the interstellar medium.

## Hydrogen Cyanide Isotopomers ( $\text{H}^{13}\text{CN}$ , $\text{HC}^{15}\text{N}$ , $\text{H}^{13}\text{C}^{15}\text{N}$ )

Hydrogen Cyanide is a linear triatomic molecule extensively studied both in laboratory and in interstellar space. An overview of HCN observations in laboratory up to the year 1974 has been published by [Maki, 1974] and is continued by [Lovas, 1978] including measurements up to 290 GHz. Later work on the ground vibrational state of the main isotopomer was published in [Ahrens et al., 2002]. Laboratory spectra for the less abundant isotopomers of HCN, particular those with more than one substituted nucleus, have been reported by [Preusser and Maki, 1993] for frequencies up to 430 GHz. Those published molecular constants formed the basis for predictions and assignments done in the presented work, including rovibrational data of [Maki et al., 2000]. Using Doppler-limited spectroscopy hydrogen cyanide displays a fairly simple rotational spectrum. However, the Cologne THz spectrometer can operate in Sub-Doppler mode, which allows measurements of the underlying hyperfine structure. The molecules have been studied in their ground state as well as in their first excited bending vibrational state  $\nu_2$  (for  $\text{H}^{13}\text{CN}$ :  $\nu_2 \approx 707 \text{ cm}^{-1}$ ). Pure rotational transitions within the first excited bending vibrational state provide in-

formation of high lying energy states which are usually accessible by IR-experiments only. The vibrational ground state consists of R-branch transitions whereas the first excited bending state exposes additional Q-branch transitions in which the removal of the degeneracy (i.e. l-type doubling) can be observed.

The presence of nuclear spins produces observable hyperfine splittings in spectra of HCN isotopomers. Those are mainly due to electric quadrupole interaction of  $^{14}\text{N}$  ( $eQq$ ) and nuclear spin-rotation interaction ( $C_I$ ) whereas the hyperfine structure caused by interaction of the H,  $^{13}\text{C}$ , or  $^{15}\text{N}$  nuclear spin could not be resolved. These unresolved splittings therefore only contribute to the broadening of the observed lines. Moreover, the nuclear spin-spin interaction term (S) was too small to be detected. The newly measured data set includes rotational transitions of  $\text{H}^{13}\text{CN}$ ,  $\text{H}^{13}\text{C}^{15}\text{N}$ , and  $\text{HC}^{15}\text{N}$  in the ground and first excited bending vibrational state up to rotational quantum number  $J = 24$ . By using the Cologne THz spectrometer a frequency accuracy of about 3 kHz has been achieved for strong transitions and thus, hyperfine structure of HCN due to the  $^{14}\text{N}$  nucleus could be resolved. Furthermore, usage of the Cologne Sideband Spectrometer for Terahertz applications (COSSTA) enabled the observation of HCN transitions up to 2 THz with high accuracy [Lewen et al., 1997].

The main isotopomer  $\text{H}^{12}\text{C}^{14}\text{N}$  is a well studied molecule in space which can be found in many interstellar sources in large abundance. Since its discovery in various types of interstellar clouds in 1971 by [Snyder and Buhl, 1971] it has been used as high density tracer ( $n_{\text{H}_2} \geq 105 \text{ cm}^{-3}$ ) in star forming regions (see [Stutzki et al., 1988] and [Lucas and Cernicharo, 1989]). However, deeper insight into HCN isotopomers like  $\text{H}^{13}\text{CN}$ ,  $\text{HC}^{15}\text{N}$ , and  $\text{H}^{13}\text{C}^{15}\text{N}$  is also of great importance since the main isotopomer often reveals opacity effects which hampers further investigations of the physical conditions within the source (see [Pirogov et al., 1995], [Goldsmith and Irvine, 1986], and [Schilke et al., 1992]). Therefore, precise measurements of these isotopomers are indispensable. Another method to study the conditions in interstellar and circumstellar environments is the use of direct l-type transitions as a probe for hot molecular gas. Recently, direct l-type transitions of the main isotopomer  $\text{H}^{12}\text{C}^{14}\text{N}$  in its first excited bending vibrational state, have been detected in interstellar space by [Thorwirth et al., 2003].

## Outline of this thesis

As has been mentioned earlier, different spectrometers have been used for the study of ethyl methyl ether as well as HCN. They are described in chapter 2. Chapter 3 gives a rough overview on asymmetric top molecules, mainly focussing on ethyl methyl ether. An explanation of internal rotation of ethyl methyl ether can be found in chapter 4 while in chapter 5 the spectral analysis of this molecule will be discussed. Chapter 6 contains theoretical considerations of linear molecules showing hyperfine structures which will be followed by a spectral analysis of the newly measured data of the hydrogen cyanide isotopomers in chapter 7. Finally, chapter 8 contains a prospect on future work based on the presented results. Due to the extensive data set obtained in this work, long tables of fitted and assigned frequencies are listed in the appendix as well as a collection of all hyperfine spectra of  $\text{H}^{13}\text{CN}$ .