

Abstract

The purpose of this work is to perform high resolution spectroscopic measurements in the terahertz region aiming at molecular parameters, derived from quantum mechanical analysis of the spectra. These parameters are the basic requirement for accurate frequency predictions and for the astronomical detections of undiscovered species. Two different spectrometers have been used for the spectral analysis in this work:

- The newly designed Supersonic Jet Spectrometer for Terahertz Applications (SuJeSTA) for the investigation of cold radicals and ions
- The Cologne Terahertz Spectrometer

The pure rotational spectra of five isotopomers of potassium chloride, i.e. $^{39}\text{K}^{35}\text{Cl}$, $^{39}\text{K}^{37}\text{Cl}$, $^{41}\text{K}^{35}\text{Cl}$, $^{41}\text{K}^{37}\text{Cl}$, and $^{40}\text{K}^{35}\text{Cl}$ have been recorded with the well established Cologne Terahertz Spectrometer. A special evaporation cell has been used to evaporate solid KCl . Within the scope of this thesis, a total of 295 new rotational lines have been measured in the frequency region between 170 and 930 GHz . For the isotopomers $^{39}\text{K}^{35}\text{Cl}$ and $^{39}\text{K}^{37}\text{Cl}$ 107 and 82, respectively, rotational transitions have been assigned to transitions belonging to vibrational levels up to the seventh excited state ($\nu \leq 7$) and to rotational quantum numbers as high as 127 and 129, respectively. 104 lines were measured for the less abundant isotopomers of $^{41}\text{K}^{35}\text{Cl}$ and $^{41}\text{K}^{37}\text{Cl}$ with $J \leq 128$, $\nu \leq 6$ and $J \leq 131$, $\nu \leq 5$, respectively. Two lines have been assigned to $^{40}\text{K}^{35}\text{Cl}$, which has a natural abundance of 0.01% relative to $^{39}\text{K}^{35}\text{Cl}$. The measured lines have been fitted together with previously published millimeter wave transitions to obtain an improved set of molecular parameters for these isotopomers. Besides this analysis, the isotopically invariant Dunham parameters U_{ij} and the Born-Oppenheimer corrections Δ_{01} have been determined. The refined and extended parameter set allows precise predictions in the terahertz region. Structural parameters, such as the bond length and the moment of inertia, have been derived from the spectroscopic parameters.

A main task of this work was the construction and assembly of the new Cologne Supersonic Jet Spectrometer for Terahertz Applications (SuJeSTA).

It is employed to record the spectra of radicals and ions which are produced in a pulsed discharge with a subsequent supersonic jet expansion to obtain adiabatically cooled molecules.

The first application of SuJeSTA has been an intensive investigation of the linear $X^2\Pi$ propynylidyne radical, $l-C_3H$. It is supposed to play a decisive role in the carbon chain growth in the interstellar medium and has been subject of astronomical observations and laboratory investigations. With SuJeSTA the ν_4 ($^2\Sigma^u$) CCH bending vibration of C_3H has been recorded in the submillimeter region for the first time. Due to a strong Renner-Teller effect the bending transitions lie in the submillimeter wavelength region. Eight measured lines have been assigned to ro-vibrational transitions between the vibrational ground state ($^2\Pi$) and the excited bending state $\nu_4 = 1$ ($^2\Sigma^u$). In addition, the pure rotational spectrum of C_3H has been investigated up to 600 GHz to extend the number of measured transitions. A total of 43 pure rotational lines in the vibrational ground states ($^2\Pi_{1/2}$, $^2\Pi_{3/2}$) and excited state $\nu_4 = 1$ ($^2\Sigma^u$) have been recorded. Reliable frequency predictions up to 1 THz are available due to a new set of spectroscopic parameters, obtained from a least squares fit to a standard Hamiltonian.

Furthermore, the new spectrometer facilitates the production of ions. In the course of this thesis, transitions of CO^+ have been recorded to prove the spectrometer's ability of ion production. An isotopically invariant fit of the new data and data published previously resulted in a mass independent parameter set which describes the spectrum of the CO^+ ion up to 1 THz with high accuracy. Improved structural constants have been derived from the spectroscopic parameters. Interstellar CO^+ is of crucial importance for tracing PDRs (Photon Dominated Region) and has been detected in space.

All obtained data are reliable for frequency predictions up to 1 THz and are available via the Cologne Database for Molecular Spectroscopy (CDMS).