

# FTMW spectroscopy of sulfur bearing free radicals, HCSC and CH<sub>3</sub>SS

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Two new sulfur bearing free radicals, HCSC and CH<sub>3</sub>SS, were observed in a discharged plasma containing CH<sub>3</sub>SH diluted in Ar, using a Balle-Flygare type Fourier transform microwave spectrometer together with a MW-MW double resonance setup. The HCSC radical is a high energy isomer of well known free radical, HCCS, about 100 kcal/mol higher in energy. Fairly strong lines with fine and hyperfine splittings were observed slightly below 16 GHz, which were assigned to  $N=1-0$ , with the  $^2\Sigma$  pattern indicating that this radical is bent, while HCCS is linear. The observation was extended to transitions with  $N=3-2$  using double resonance. So far only  $K_a=0$  transitions were observed. Although the signals of HCSC were strong with the present precursor, those of HCCS were very weak.

In addition to the lines of HCSC, lines with very complicated splittings were observed extending in the region 16 GHz to 18 GHz, which were finally assigned to transitions of CH<sub>3</sub>SS. The CH<sub>3</sub>SS radical has a bent CSS structure with internal rotation of the methyl top. Thus, this species consists of a series of open shell radicals, CH<sub>3</sub>OO, CH<sub>3</sub>SO, and CH<sub>3</sub>SS, where FTMW spectra have been observed for the former two species (K. Kato *et al.*, unpublished). A number of lines have been observed with  $N_{\text{up}}$  to 4 with  $K_a=0$  and 1, for  $a$ - and  $b$ -type transitions. Splittings due the spin-rotation interaction, the proton hyperfine interaction, and the  $A/E$  splittings due to internal rotation of the methyl top have been observed for this species, which were analyzed by the Hamiltonian for open shell species with internal rotation. The present data together with those of CH<sub>3</sub>OO and CH<sub>3</sub>SO may provide invaluable data for deeper understanding of the energy levels of open shell species with internal rotation, which have not been studied well so far.

# Millimeter-wave spectroscopy of the HDCCH radical

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The vinyl radical,  $\text{H}_2\text{CCH}$ , has a proton tunneling motion of  $\alpha$ -proton governed by a double minimum potential with barrier height of  $1580\text{ cm}^{-1}$ [1]. The ground state splits into a doublet ( $0^+$  and  $0^-$ ) and the proton tunneling transitions between the  $0^+$  and  $0^-$  levels have been observed by MMW spectroscopy[1, 2]. If one of the  $b$ -proton is deuterated, the effective 1-D potential for the  $\alpha$ -proton bending motion becomes to be asymmetric due to the zero point vibrations of  $b$ -deuteron. The proton tunneling is hindered and the  $b$ -type rotational transitions of  $\Delta K_a = \pm 1$  will be observed within the *cis*- and *trans*-tautomers instead of the tunneling transition, where *cis*-HDCCH has an unpaired electron on the same side of deuterium with respect to the C=C double bond, while *trans*-HDCCH on the opposite side.

In the present study, the HDCCH radical produced by the 193 nm excimer laser photolysis of HDCCHCl have been observed by MMW spectroscopy combined with a pulsed supersonic jet technique. The  $b$ -type rotational transitions of  $N_{K_a, K_c} = 1_{11} - 0_{00}$ ,  $2_{12} - 1_{01}$ ,  $1_{10} - 1_{01}$ , and  $2_{11} - 2_{02}$  as well as the  $a$ -type transitions of  $2_{02} - 1_{01}$  and  $3_{03} - 2_{02}$  were observed for one tautomer in the frequency region of 100 – 260 GHz.

Observed  $A_0$  rotational constant, 183.3340 GHz, is close to that for *cis*-HDCCH (181.3 GHz) rather than that for *trans*-HDCCH (165.8 GHz) given by a CCSD(T)/aVTZ level calculation. The  $\gamma$  angle, between the principal axes of the observed magnetic dipolar interaction and the molecule-fixed axes, was calculated to be  $29.3(26)^\circ$  confirming the observed HDCCH radical is the *cis*-HDCCH ( $\gamma=28.9^\circ$ ) but not the *trans*-( $\gamma=37.6^\circ$ ) form. Observed Fermi contact interaction constants for the  $b$ -proton ( $a_F=176.45\text{ MHz}$ ) and  $b$ -deuteron ( $a_F=16.66\text{ MHz}$ ) are also consistent with the estimated values (184.7 and 17.0 MHz) for *cis*-HDCCH from the hyperfine constants obtained by the ESR study in the Ar matrix [3]. The rotational spectra of the *trans*-HDCCH, however, have not been observed in supersonic jet. The zero point energy gap  $\Delta_{\text{tco}}$  between the *trans*- and *cis*-tautomers estimated to be  $33\text{ cm}^{-1}$  by the *ab initio* calculation is large enough only the *cis*-HDCCH tautomer is populated in the supersonic jet condition ( $T \approx 15\text{ K}$ ).

[1] JCP, 120, 3604 (2004). [2] Mol. Phys., 108, 2289 (2010). [3] JACS, 94, 5950 (1972).

# Accurate rotational fingerprints of radioactive radicals by mass-independent studies on AlO, TiO, and FeO

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Astrophysical observation of radioactive isotopes, like  $^{26}\text{Al}$ ,  $^{44}\text{Ti}$ , or  $^{60}\text{Fe}$ , provide insight into the nucleosynthesis processes of stellar cores[1]. The detection of characteristic photons which are released during radioactive decay is used to map their spatial distribution on large scale[2]. In general, the assignment to certain stellar objects fails due to limited sensitivity, exceptions are the nearby supernovae remnants *Cas A*[3] and *SN1987A*[4] for which the radioactive nucleus  $^{44}\text{Ti}$  was detected.

An alternative approach to detect radioactive isotopes is to observe abundant molecules containing radioactive isotopes. This enables spectroscopic observation of rotational transitions by radio-telescope facilities, like *ALMA*. In the environment of stellar objects, the molecular condensation starts with simple diatomic particles containing oxides of refractory elements.

The astrophysical detection of diatomic radioactive molecules requires highly accurate rotational transition frequencies, which can be obtained from laboratory measurements of stable isotopologues and by applying the Dunham approach[5] to obtain scaled frequencies of radioactive isotopologues.

In this work, systematic studies are presented for  $^{26}\text{AlO}$ ,  $^{44}\text{TiO}$ , and  $^{60}\text{FeO}$ , as most promising stellar tracers of nucleosynthesis, based on high-resolution measurements on the rotational transitions of their abundant stable isotopologues ( $^{27}\text{Al}$ ,  $^{46-50}\text{Ti}$ ,  $^{54,56-58}\text{Fe}$ ). Experiments were performed when a solid target (Al, Ti, Fe) is evaporated by a pulsed laser into an oxygen-rich buffer gas to form simple metal oxides. Adiabatically planar expansion of the gas jet into a vacuum chamber cools the gas to a few tens of Kelvin and subsequently, Doppler-free rotational absorption spectra are recorded in the frequency range up to 400 GHz.

A global data analysis, which also includes results from the literature, reveals the molecular structure beyond the Born-Oppenheimer (BO) limit, resulting in experimentally derived BO correction coefficients of these metal oxides for the first time. Based on this analysis, the rotational transitions of the radioactive molecules are determined with high accuracy at the sub-MHz level, which enables their unambiguous identification in stellar environments.

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[2] R. Diehl et al., *Nature*, 2006, 439, 45

[3] B. W. Grefenstette et al., *Nature*, 2014, 506, 339

[4] S. E. Boggs et al., *Science*, 2015, 348, 670

[5] J. L. Dunham, *Phys. Rev.*, 1932, 41, 721

# Accurate sub-millimeter rest-frequencies for HCCO and DCCO radicals

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The ketenyl radical, HCCO, has been one missing link in interstellar oxygen-bearing chemistry, since it has been detected in only two starless cores so far. Its measured abundance is three orders of magnitude higher than predicted, meaning that there is one powerful formation mechanism still unknown. Moreover, its deuterated counterpart, DCCO, has never been identified in the ISM. HCCO and DCCO still lack of precise spectroscopic investigation although they exhibit a significant astrophysical relevance.

The present work has expanded the study of the ground-state pure rotational spectra of HCCO and DCCO into the sub-millimeter region.

The spectra acquisition was done with a frequency-modulation absorption spectrometer between 170 and 750 GHz. The radicals were produced in a low-density plasma by applying a negative glow discharge. For each isotopologue we were able to detect and assign more than 100 rotational lines.

The new measured lines have substantially increased the previous data set allowing the precise determination of high order rotational and centrifugal distortion parameters. In our analysis we take into account the Renner-Teller interaction between the ground state and a low lying excited state, enabling the prediction and assignment of up to  $K_a=4$  rotational transitions.

The new set of spectroscopic parameters provide highly accurate, millimeter rest-frequencies of HCCO and DCCO for future astronomical observations. These results are very promising for a DCCO detection toward a starless core.

# Terahertz spectroscopy of isotopologues of amidogen radical

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Amidogen is an asymmetric-top free radical that belongs to the nitrogen-hydrides family and it plays an important role as intermediate in the synthesis of interstellar ammonia.

The main isotopologue  $\text{NH}_2$  and its  $^{15}\text{N}$ -substituted variant have already been detected in the space, while no astronomical observations of the deuterated species of amidogen have been reported to date. In the last year, we focused our research activity on the study of the rotational spectrum of several deuterated isotopologues of amidogen radical, namely  $\text{NHD}$ ,  $\text{ND}_2$ ,  $^{15}\text{NHD}$ , and  $^{15}\text{ND}_2$ .

For the two former species, the measurements of the ground state spectrum was extended to the THz region and the newly recorded transitions were analyzed together with the literature data.

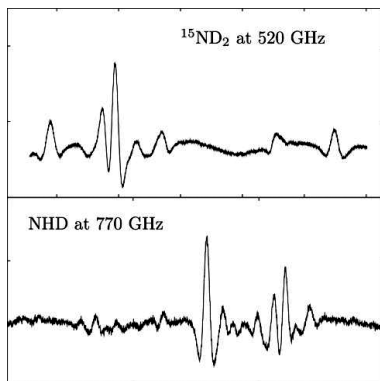
On the other hand, no laboratory detection for  $^{15}\text{NHD}$  and  $^{15}\text{ND}_2$  were reported so far and their pure rotational transitions have been observed for the first time from millimeter-wavelength to THz frequencies.

The recorded spectra show a fine-structure due to the electronic spin ( $S = 1/2$ ) that couples with the rotational angular momentum ( $J = N + S$ ) and a hyperfine-structure due to the nuclear spins  $I_{\text{H}}$ ,  $I_{^{15}\text{N}} = 1/2$ ,  $I_{\text{D}}$ ,  $I_{\text{N}} = 1$ .

As example, a record of one fine-component of the  $1_{11} - 0_{00}$  transition for two isotopologues is reported in Fig. 1.

The differences between the spectra have to be ascribed to two factors: (i) the magnetic hyperfine-constants whose value varies from isotope to isotope and (ii) the appropriate symmetry combinations of rotational and nuclear wavefunctions.

Indeed, since deuterium is a boson, the total molecular wavefunction must be symmetric upon the exchange of two identical nuclei only for the symmetric species  $\text{ND}_2$  and  $^{15}\text{ND}_2$ .



# Accurate rotational frequencies of deuterated Ammonium ions ( $d_1$ – $d_3$ ) measured in a cryogenic ion trap

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Two of the most abundant nitrogen-bearing molecules in the interstellar medium are  $N_2$  and  $NH_3$ . Their protonated ions  $NH_2^+$  (diazenylium) and  $NH_4^+$  (ammonium) can provide critical information on interstellar chemistry. While  $N_2H^+$  has been observed in many different sources, and it is, in fact, used as a proxy for  $N_2$ ,  $NH_4^+$  being non-polar, cannot be observed through its rotational transitions. Nevertheless, it is predicted to be very abundant, since the proton affinity of  $NH_3$  is very high, and it remains stable against collisions with the abundant  $H_2$ . However, deuterated variants of  $NH_4^+$  ( $d_1$ – $d_3$ ) do possess small permanent dipole moments, and could be detected via rotational transitions. In fact,  $NH_3D^+$  has been detected in space in Orion IRc2 and in the cold core B1–bS through its transition  $J_K=1_0-0_0$  [1]. At the time of its detection, there were no laboratory data on the rotational spectroscopy of  $NH_3D^+$  and the rest frequency was derived from an analysis of the high resolution IR spectrum of the  $\nu_4$  band [2]. The frequency was confirmed later by an accurate direct measurement in the mm-wave in a cryogenic ion trap in the Cologne laboratories [3]. In order to provide accurate rest frequencies for the other polar isotopologues, experiments have been performed in a cryogenically cooled ion trap using the state-dependent attachment of He atoms to ions as an action spectroscopy technique. Improved frequencies for  $NH_3D^+$  as well as first direct measurements for  $NH_2D_2^+$  and  $NHD_3^+$  (guided by recent work by the group of D. Nesbitt [4]) have been obtained.

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[2] Doménech et al. 2013 ApJL 771, L11

[3] Stoffels et al. 2016 A&A 56, 1

[4] Chang et al. 2018 JCP 148, 014304