# Microwave spectrum and equilibrium structure of Diphenyl Disulfide

Jean Demaison[1], **Rizalina T. Saragi**[2], **Marcos Juanes**[2], **Natalja Vogt**[1], **Alberto Lesarri**[2]

1) *Section of Chemical Information Systems, University of Ulm, Albert–Einstein–Allee 47, 89081 Ulm*

2) *Departamento de Química Física y Química Inorgánica, Facultad de Ciencias, Universidad de Valladolid, Paseo de Belén, 7, 47011 Valladolid*

The disulfide bridge ($-S-S-$) is an important structural motif in organic and protein chemistry, so the determination of accurate equilibrium structures is well justified. Diphenyl disulfide ($C_6H_5-S-S-C_6H_5$, DPDS, see figure) is widely used in organic synthesis and a challenging target since its structure is determined by 34 independent parameters. We report supersonic–jet microwave measurements of the rotational spectra of DPDS (including all ^{13}C and ^{34}S isotopologues) and the determination of the equilibrium structure by the mixed estimation (ME) method. A single conformer of C_2 symmetry was observed in the gas–phase. In order to estimate the equilibrium structure of this conformer, the mass–dependent r_m method was used to fit the structural parameters concurrently to predicate parameters and moments of inertia, affected with appropriate uncertainties. The predicate parameters were obtained by high–level quantum–chemical computations. A careful analysis of the results of different fits and a comparison with the ab initio optimizations confirms the validity of the used methods. The most interesting part of the structure of DPDS is the S–S bond. The $r(S–S)$ bond length at 2.020 Å is very similar to the value found in $HSSH_{anti}$ (2.022 Å) but significantly shorter than in CH_3SSCH_3 (2.033 Å). The $r(C–S)$ bond length at 1.776 Å is rather short. The bond angle C–S–S is 105° (102.1° in CH_3SSCH_3). The dihedral angle τ(C–S–S–C) at 82.6° shows differences with previously known values (CH_3SSCH_3: 84.8, $HSSH_{anti}$: 90.6°; in $HSSOH_{anti}$ 84.8° and in $HSSOH_{syn}$. 99.4°). Finally, the deformation of the benzene ring is also worthy of note. Full structural details will be reported at the Conference.
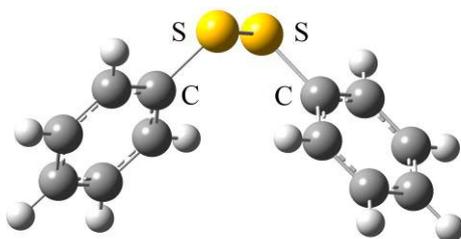
# Semi–experimental structure of vinyl acetate determined by microwave spectroscopy and ab initio methods

Stefanie Genuit[1], **Sven Herbers**[1], **Daniel Adam Obenchain**[1], **Jens–Uwe Grabow**[1]

1) *Leibniz Universität Hannover*

Vinyl acetate is a well–known molecule in the field of gas–phase spectroscopy. For example Velino et al. (2009) [2] and Nguyen et al. (2014) [1] show transitions in the frequency region from 64 to 78 GHz [2] and 7 to 37 GHz [3] respectively. Kolesniková et al. (2015) [3] further investigated the existence of vinyl acetate in the interstellar area of Orion KL. The presented project is the first to aim for accurate structure determination from isotopologue data of vinyl acetate.

The microwave spectrum of vinyl acetate was investigated in the region from 8.3 to 27.3 GHz using the IMPACT (in–phase/quadrature–phase–modulation passage–acquired–coherence technique) spectrometer [4]. Higher resolution measurements in areas of interest were carried out with the CO–BRA–FTMW (multioctave coaxially oriented beam–resonator arrangement Fourier–transform microwave) spectrometer [5]. Vinyl acetate contains a methyl group and its internal rotation couples to the overall rotation which leads to notable splittings in the rotational spectrum. The fit of molecular parameters to the experimental spectrum was carried out utilising the XIAM [6] program assuming C_s symmetry.

Several of the strongest transitions of the parent molecule were observed for ^{13}C and ^{18}O isotopologues in natural abundance as well. From the rotational constants of the isotopologues and with the help of ab initio methods the semi–experimental equilibrium structure of vinyl acetate was determined.
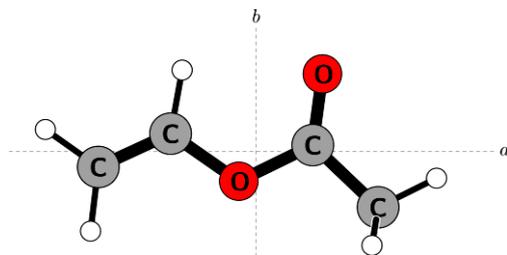
[1] J. Phys. Chem. A, 2014, 118, 12130,
[2] J. Mol. Spec., 2009, 256, 228
[3] A&A, 2015, 577, A91
[4] J. Mol. Spec., 2012, 280, 54
[5] Rev. Sci. Instrum., 1996, 67, 4072
[6] Z. Naturforsch 1996, 51a, 923

Pure rotational spectrum of $^{(15)}$ND and isotopic–independent Dunham–type analysis of imidogen radical

Luca Bizzocchi[1], Mattia Melosso[2], Filippo Tamassia[3], Luca Dore[2], Claudio Degli Esposti[2], Elisabetta Canè[3]

1) *Center for Astrochemical Studies, Max–Planck–Institut für extraterrestrische Physik, Giessenbachstr. 1, 85748 Garching bei München (Germany)*

2) *Dipartimento di Chimica "Giacomo Ciamician", Università di Bologna, Via F. Selmi 2, 40126 Bologna (Italy).*

3) *Dipartimento di Chimica Industriale "Toso Montanari", Università di Bologna, Viale del Risorgimento 4, 40136 Bologna (Italy)*

The rotational spectrum of ^{15}ND in its ground electronic $X^3\Sigma^-$ state has been recently observed in the Bologna laboratory.

The radical has been generated in a glow discharge of a mixture of ^{15}N$_2$ and D$_2$ in Ar as a buffer gas. Thirty–four hyperfine components belonging to the ground vibrational state and 9 components for the $v = 1$ state have been recorded with a frequency–modulation millimetre–/submillimetre–wave spectrometer. They include the complete fine–structure of the $N = 1 \leftarrow 0$ transition and the strongest fine–components of the $N = 2 \leftarrow 1$ transition for the ground state (see Figure 1), and the $\Delta J = 0, +1$ components of the $N = 1 \leftarrow 0$ transition for the $v = 1$ state.

These new isotopic measurements complete the high–resolution spectroscopy characterisation of the imidogen radical: presently, all four stable isotopologues, i.e., NH, ND, ^{15}NH and ^{15}ND, have been studied in the millimetre, and/or infrared domains. The resulting, extensive data set have been analysed using a multi–isotopologue Dunham model to represent the ro–vibrational, fine, and hyperfine energy contributions. The least–squares fit was performed on a sample of more than 1500 transitions, yielding a comprehensive set of isotopically independent U_{lm} parameters plus 13 Born–Oppenheimer Breakdown coefficients Δ_{lm}. As alternative approach, we performed a Dunham analysis in terms of the most abundant isotopologue coefficients Y_{lm} and some isotopically dependent Born–Oppenheimer Breakdown constants δ_{lm} [R. J. Le Roy, *J. Mol. Spectrosc.* **194**, 189 (1999)]. The two fits provide results of equivalent quality.

The Born–Oppenheimer equilibrium bond distance for imidogen radical has been calculated yielding r_e^{BO} = 103.606721(13) pm and the zero point energies have been derived for all isotopologues. Additionally, the adiabatic correction to the equilibrium distance have been determined from purely experimental data and compared to a value estimated using high–level *ab initio* calculations.
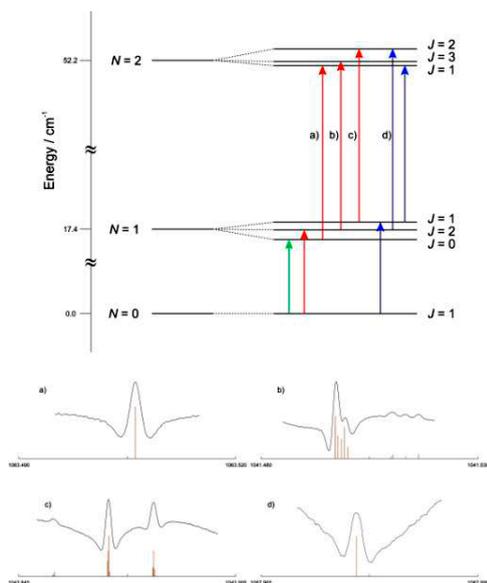
Rotational spectroscopy of the two higher energy conformers of 2–cyanobutane

Marius Hermanns[1], **Nadine Wehres**[1], **Frank Lewen**[1], **H.S.P. Müller**[1], **Stephan Schlemmer**[1]

1) 1. Physikalisches Institut – University of Cologne

We present high–resolution rotational spectroscopy of two out of three conformers of 2–cyanobutane. Spectra were taken between 10–26 GHz by means of chirped–pulse spectroscopy. Spectra between 36 and 402 GHz were recorded by means of frequency modulated (FM) absorption spectroscopy. The analysis yields precise rotational constants and higher order distortion constants, as well as a set of 14N nuclear electric quadrupole coupling parameters. In addition, quantum chemical calculations were performed assisting the assignments. Calculations of vibrational frequencies yield insight into the vibrational energy structure from which partition functions and vibrational correction factors are determined. These are used to determine experimentally and computationally the energy difference between the conformers. Overall, this study provides precise spectroscopic constants for the search of 2–cyanobutane in the interstellar medium. In particular, this molecule appears as an interesting case to test our knowledge of (branched) molecule formation in space.

A6.4.