

MILLIMETRE-WAVE SPECTROSCOPY OF REACTIVE MOLECULES IN ELECTRICAL DISCHARGE - STUDY OF H₂SiO

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A multitude of ions, radicals and other short-lived reactive species can be formed by electrical discharge in a low pressure gas mixture. A study of these reactive species is crucial for a good understanding of the numerous chemical and physical processes taking place in the atmosphere and in certain regions of space. Laboratory measurements of millimetre-wave rotational spectra of these species can identify their presence in these non-accessible regions. The experimental and theoretical challenges posed by this work as well as its interest are well illustrated by the recent discovery of H₂SiO in a plasma of silane and oxygen. Several known and unknown species have been formed in this plasma and their overlapping spectra complicates identification. Only by means of a recently developed method for measuring the lifetime of each of these species was it possible to extract the spectrum of H₂SiO. This method consists of modulating the discharge (on/off) and detecting the resonant absorption signal as a function of time using a digital oscilloscope. The spectrum of H₂SiO shows some interesting effects. Close-lying K_a doublets are less split than predicted and when very close-lying show a spectral profile indicating the presence of four lines, the two small additional lines corresponding to non-allowed transitions. Measurements of the ¹⁸O, ²⁹Si, ³⁰Si and D isotopic species permit an accurate calculation of the equilibrium structure for comparison with ab-initio calculations. A very rich residual spectrum observed simultaneously with H₂SiO has not yet been identified and may include the spectra of the two species HSiOH cis and trans which are predicted to lie at the same energy as H₂SiO.

H2

DETECTION AND STRUCTURE OF CARBON-CHAIN MOLECULES, C_nO ($n=2,4\sim 9$), BY PDN-FTMW SPECTROSCOPY

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Rotational spectra of C_nO ($n=2, 4 \sim 9$) have been observed by using a Fabry-Perot type Fourier transform microwave (FTMW) spectrometer cooperated with a pulsed discharge nozzle (PDN). The molecules have been generated by a pulsed electric discharge of C_3O_2 diluted in Ar, and then adiabatically cooled to ≈ 2 K in a subsequent supersonic expansion. The molecules with odd n exhibit a spectrum characteristic of a linear-molecule in a singlet electronic state. For the C_5O molecule, spectra of the normal and all the single isotope substituted species have been assigned, leading to a substitution structure. The r_s -structure and the structure calculated by an *ab initio* MO theory for the C_5O molecule has been compared and the linearity of the molecule has been discussed. The average C-C bond lengths in the C_7O and C_9O molecules have been calculated by assuming the same partial structure as that in the C_5O molecule.

The molecules with even n have been analyzed as linear molecules in the $^3\Sigma^-$ electronic ground state. The determined molecular constants, such as rotational, spin-spin coupling, and centrifugal distortion constants, have been provided information on the C=C bond length, energy gaps between the excited $^1\Sigma^+$ electronic state and the $^3\Sigma^-$ ground state, and rigidity of the molecules in respect of the bending vibration.

FREE JETS MILLIMETER-WAVE SPECTROSCOPY IN BOLOGNA

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We have recently set up a millimeter wave free jet spectrometer. Its source is a KVARZ millimeter-wave synthesizer working in the frequency range 53.6-78.3 GHz and the radiation is focalized on the jet plume with a lens corrected horn system purchased from Montech (Clayton, Australia).

We have used it, as first applications, for the study of conformational equilibria in some complicated cases, not resolved so far by conventional microwave spectroscopy:

(a) Three conformers have been detected for 1-chloro-butane. The simplification of the spectra inherent the free jet expansion has allowed easy assignments of the various conformers.

(b) The syn conformer has been assigned for allyl alcohol. The rotational spectrum of the skew conformer of allyl alcohol has been reported earlier (1), while the wide doublings due to the internal rotation of the hydroxyl group prevented the assignment of the spectrum of the syn conformer.

In both cases a mixture of the sample in Argon (7%) at a stagnation pressure of 0.2 atm at room temperature was expanded to a final pressure of 10^{-3} torr through a nozzle with a diameter of 0.35 mm.

Reference:

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Infrared Laser Spectroscopy of Jet-Cooled Carbon Clusters: The Spectra of C₁₃ and SiC₃Si

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Pure carbon clusters and silicon-carbon clusters have been of interest for many years due to their astrophysical importance but also because of the different isomers that occur with increasing cluster size.¹ In the case of small carbon clusters that contain less than 10 atoms *ab initio* calculations predict for *odd* numbered clusters a linear $^1\Sigma$ electronic ground state bonding while for even numbered clusters two low energy structural isomers - a $^3\Sigma$ linear chain and a singlet cyclic ring are possible. The Berkeley supersonic cluster beam apparatus for mid-infrared diode laser spectroscopy² has been applied to the first gas phase characterization of linear C₄, C₅, C₆, C₇ and C₉. No spectroscopic evidence for the cyclic isomer of any even cluster currently exists.

For all clusters in the intermediate size range, containing 10 - 20 carbon atoms a ring structure is predicted to be more stable than the linear form for both even and odd numbered clusters. With C₁₃ we present the first high resolution spectrum of a pure carbon cluster in this size range. More than 70 absorption lines of an asymmetric stretching band have been measured with the band origin at 1809 cm⁻¹. The data fit perfectly to a *linear* molecule.

We also present a gas phase spectrum of linear SiC₃Si. The band origin was found to be at 1969 cm⁻¹. For both molecules the rotational constants for the ground state and the first vibrational excited state were obtained by a least squares fit.

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1. Weltner and Van Zee, *Chem. Rev.* **89**, 1713 (1989).

2. J. R. Heath and R. J. Saykally, *J. Chem. Phys.* **94**, 1724 (1991).