Millimeter wave spectroscopy of transient species in RF and DC discharges.

J.L. DESTOMBES

Laboratoire de Spectroscopie Hertzienne, associé au CNRS Université de Lille I, 59655 VILLENEUVE D'ASCQ CEDEX.

Millimeter wave spectra of free radicals and molecular ions are observed in a liquid nitrogen cooled RF or DC discharges. Recent results on CO+, CH, 13CN, H2D+ and HCO2+ are reviewed.

Since the first detection of a molecular ion by WOODS and coworkers [1], DC discharges are currently used to produce transient species of very short lifetime.

In Lille we have developed an electrodeless discharge excited by a radiofrequency self oscillator. The absorption cell is 1 m long and can be cooled to liquid nitrogen temperature. In situ discharges are easily ignited in a large pressure range, from some mtorr to several hundred mtorr and they are generally very quiet. The maximum power density attainable is 0.15 W cm−2. As expected, the rotational temperature is near the wall temperature. But the vibrational temperature is always very high for example, rotational spectrum of CN has been observed up to v = 11.

A number of interesting species can be efficiently produced in this discharge, including some molecules of astrophysical interest = CO+, CH, CN, HCS+, HCCN, ...

1) The CO+ molecular ion is easily produced by discharging pure CO at low temperature. The analysis of 4 isotopic substitutions in ground and vibrational states led us to the determination of the equilibrium structure and to the study of the breakdown of the Born-Oppenheimer approximation [2].

2) CH was known in the IS medium for about 10 years but its microwave spectrum was not known in the laboratory. We have been able to detect several transitions of this radical [3]. In a
parallel work done at the same time, J. BROWN detected other transitions by Microwave Optical Double Resonance [4]. All these results have been used to predict unobserved transitions of astrophysical interest, and some of them have been recently detected [5].

3) In addition to the \( J = 1 - 2 \) transition of HCS\(^+\) observed by C. WOODS and coworkers [6], we have measured 5 successive rotational transitions of this ion first detected in the IS medium [7]. This is a definitive confirmation of the identification of this species. This was not obvious since discharge in \( \text{H}_2\text{S} + \text{CO} \) give rise to a number of unidentified lines and then to possibilities of fortuitous coincidences [8].

4) Owing to the presence of two nuclear spins, the hyperfine structure of the \(^{13}\text{CN} \) radical is complicated and we have for example measured 41 components for the two first rotational transitions. Using our analysis [9], French radioastronomers have recently detected \(^{13}\text{CN} \) in three IS sources [10].

More recently we have developed another type of discharge which is a negative glow discharge extended by a magnetic field. This technique has been applied to millimeter wave spectroscopy by FC de LUCIA and coworkers [11].

Using a predicted frequency kindly provided by T. AMANO, we have detected the \( \text{1}_{11} - \text{1}_{10} \) submillimeter transition of \( \text{H}_2\text{D}^+ \) at 372421.34 (20) MHz. The best results have been obtained in an Ar discharge with traces of \( \text{H}_2 \) and \( \text{D}_2 \) [12].

We have also observed the \( K = 0 \) and \( K = 2 \) components of two successive rotational transitions of the protonated carbon dioxide \( \text{HCO}_2^+ \) [13]. These lines fit very well with the IS lines observed by THADDEUS and coworkers some years ago [7]. This is a confirmation that the IS lines are due to \( \text{HCO}_2^+ \) and not to the \( \text{HOCN} \) isoelectronic molecule. The observation of \( \text{HCO}_2^+ \) is then an indirect detection of \( \text{CO}_2 \) in the IS medium. This is the second example of a non polar molecule detected through its protonated form.

REFERENCES.