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Millimeterwave spectroscopy of transient molecules produced in a DC discharge

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Abstract. The construction of a millimeterwave spectrometer to study the pure rotational spectra of transient molecules in the gas phase is presented. The spectrometer is a source-modulated system combined with a free space glass discharge cell. Millimeterwave radiation has been produced using a frequency multiplier, the fundamental radiation source being klystrons. The spectrometer has been used to study the millimeterwave spectrum of carbon monosulfide (CS) and fluorine cyanide (FCN) produced inside the cell in a low pressure DC discharge of precursor gases. The quadrupole hyperfine structures of ^{33}S and ^{14}N nucleus of CS and FCN have been resolved, measured and analysed.

Keywords. Millimeterwave spectroscopy; transient molecule.

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1. Introduction

Studies on transient molecules, e.g., molecular ions, free radicals and other unstable molecules by microwave/millimeterwave spectroscopic technique have made substantial amount of progress during the last three decades or so after a shaky start. The initial slow progress was due to the problem of handling these species because they are chemically active in nature and it was not so easy to produce them in high concentration in gas phase in the laboratory. However, sustained efforts by several groups of laboratory spectroscopists have made it possible to generate and study transient molecules in the laboratory. Dousmanis *et al* [1] observed several Λ-type doubling transitions of OH, a free radical produced by a discharge in low pressure water vapour outside the cell. Almost a decade later, the second transient molecule, SO was detected by Powell and Lide [2] and Winnewisser *et al* [3]. SO radical was also produced outside the cell by reactions of discharged oxygen with OCS, H_2S or solid sulphur. The initial hesitation of making DC discharge inside the absorption cell was overcome by Woods [4] who developed a free space absorption cell and showed that transient species can be produced by a low pressure DC discharge inside the cell without affecting the detection system of the spectrometer. Dixon and Woods [5] detected the rotational spectra of CO^+ ion which was the first molecular ion detected by

laboratory microwave spectroscopy. Since then, many transient molecules have been produced and studied in the laboratory [6,7]. Radio astronomers have so far detected more than hundred stable and transient species in the interstellar space [8].

In the present communication, the construction of a millimeterwave spectrometer to study transient molecules in the gas phase has been presented. Using this spectrometer the millimeterwave spectrum of carbon monosulphide (CS) and fluorine cyanide (FCN) have been observed. CS and FCN are both unstable in nature and were produced inside the absorption cell using a low pressure DC discharge of some precursor gases. The ^{33}S and ^{14}N nuclear quadrupole hyperfine structures of CS and FCN have been resolved and analysed.

2. Construction details

The spectrometer is basically a source-modulated system combined with a free space glass discharge cell of 1 m length and 10 cm diameter. The cell is fitted with two teflon lenses and two side glass ports for sample flowing. The teflon lens serves as vacuum windows at each end. Two tungsten wires are inserted through two top ports by means of a glass metal joint and two cylindrical stainless steel electrodes are pushed inside the glass cell. The outer diameter of the stainless steel electrodes have been made exactly identical with the inner diameter of the glass cell so that they fit tightly together inside the cell. The length of the tungsten wires has been adjusted so that the bottom end of the wires makes good contact with the electrodes. The top ends of the two tungsten wires have been used to apply DC voltage along the cell to start the discharge of a gas or a mixture of gases inside the cell. A high voltage DC regulated power supply (6 kV, 1300 mA, Glassman, Japan) has been used for this purpose. Using the DC discharge method, transient molecules of chemical and astrophysical interest, e.g., molecular ions, free radicals and other unstable molecules can be generated inside the cell. Furthermore, an enamelled copper wire of 2 mm diameter has been wound around the cell and connected to another DC regulated power supply (100 V, 10 A) to generate magnetic field inside the cell. This enables us to distinguish paramagnetic lines from the lines of neutral species. An arrangement of flowing liquid nitrogen vapour from a pressurized liquid nitrogen vessel through a copper jacket surrounding the cell has been made to cool the entire cell during continuous operation of the spectrometer. The cell has been connected with a Hind High Vacuum pumping system (model VS 150).

Millimeterwave radiation has been produced by using a frequency doubler (Millitech Model MUD-15-H23FO), the fundamental radiation source being klystrons (OKI 24V10A, 30V10, 35V10) covering the frequency range 22.0–37.0 GHz. Millimeterwave radiation is fed into the free space absorption cell by a waveguide horn and teflon lens. A similar horn and lens arrangement is used to focus the millimeterwave power onto the detector after propagating through the cell. The klystron is frequency-modulated by a double-square-wave of 50 kHz [9] and the signal from the detector (Millitech Model DBT-15-RP000) is amplified by a 100 kHz tuned pre-amplifier and detected by a phase-sensitive lock-in-amplifier (Princeton Applied Reseach Model 124A) in the $2f$ mode. The output of the lock-in-amplifier is fed directly to an oscilloscope or a chart recorder for signal display. The uncertainty in frequency measurement has been estimated to be ± 0.15 MHz. A block diagram of the spectrometer is shown in figure 1.

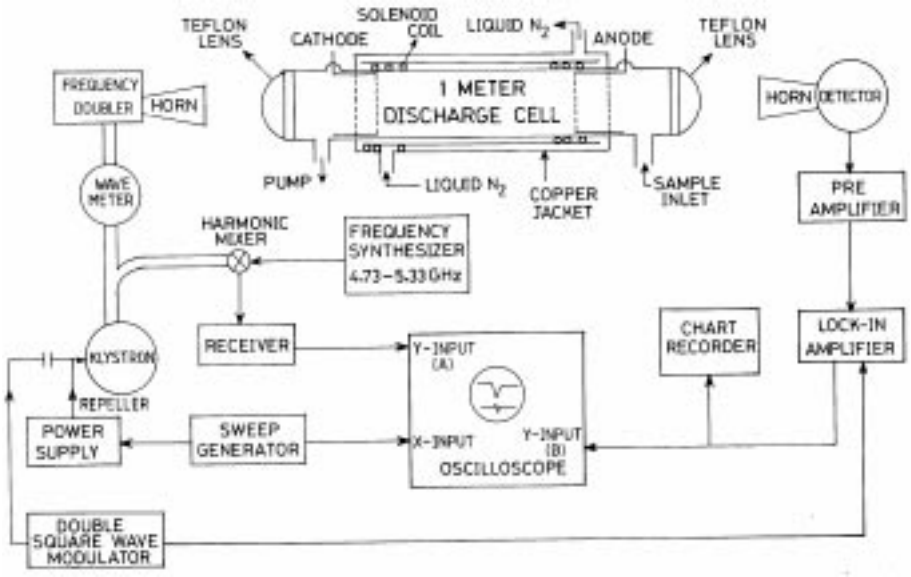

Figure 1. Block diagram of the millimeterwave spectrometer.

3. Observations

3.1 *Millimeterwave spectrum of carbon monosulfide (CS)*

Rotational lines of CS and several of its isotopic species in the millimeterwave region were observed in an rf discharge in CS_2 by several workers [10–12]. Hence, precise values of transition frequencies are well-known. With the spectrometer described in the previous section, we have been able to observe several millimeterwave rotational transitions of CS and some of its isotopic species. Carbon monosulfide (CS), an unstable diatomic molecule, was produced inside the free space absorption cell by passing low pressure (20–30 mTorr). CS_2 through a DC discharge. The discharge current was maintained at around 50 mA. In order to observe the $J = 0 \rightarrow 1$ transition of the vibrational ground state $(v = 0)$ which is at 48990.978 MHz [12], the fundamental klystron frequency was set at 24495.50 MHz and a saw-tooth voltage was applied to the repeller end of the klystron which enables the klystron frequency to sweep a couple of MHz around the centre frequency. Once the frequency selection is complete the high voltage DC regulated power supply was switched on and a DC discharge was applied inside the cell through which low pressure flow of CS_2 had been maintained. Immediately, a strong signal appeared on the oscilloscope screen which corresponds to the $J = 0 \rightarrow 1$ transition of $^{12}C^{32}S$. The signal was measured with the second harmonic of the klystron fundamental frequency. Another weaker signal, which appeared in the higher frequency side of the previous one, when measured with the fourth harmonic of the klystron frequency corresponded to the $J = 1 \rightarrow 2$ transition of the same species $^{12}C^{32}S$. A similar type of spectrum was reported by Kewley *et al* [10] with the third and sixth harmonic of the klystron fundamental frequency for $J = 1 \rightarrow 2$ and $J = 3 \rightarrow 4$ transition at 97981.007 MHz and 195954.162 MHz respectively. The spectrum

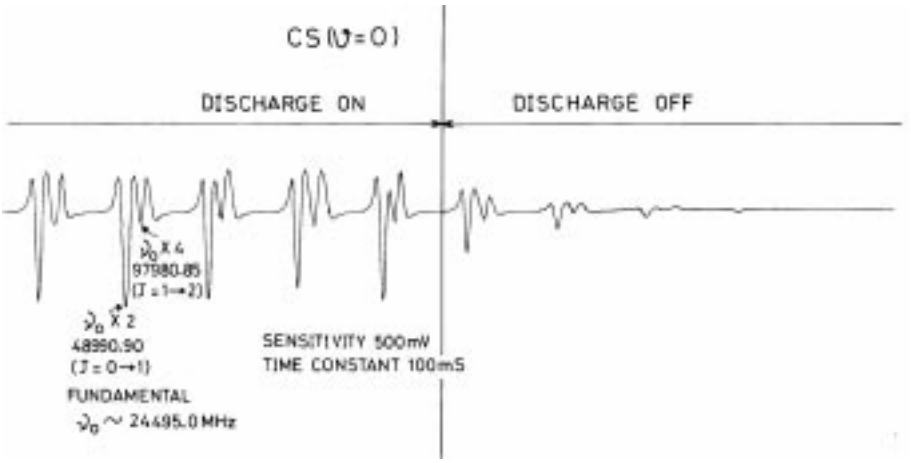

Figure 2. $J = 0 \rightarrow 1$ and $J = 1 \rightarrow 2$ transitions of $^{12}C^{32}S$ at 48990.90 MHz and 97980.85 MHz respectively using the second and fourth harmonic of klystron fundamental frequency (lock-in amplifier sensitivity = 500 mV, time constant = 100 mS).

recorded with the present set-up is shown in figure 2. The spacing between the two lines is due to the different centrifugal distortion terms for the two rotational transitions. It may be seen in figure 2 that the repetitive signal gradually diminishes in intensity after the DC discharge was switched off while the flow of the gas continues. This indicates the transient nature of CS. Subsequently, the signals belonging to the $J = 0 \rightarrow 1$ transition of the first and second excited vibrational state $(v = 1, 2)$, signals of other isotopic species of CS e.g., $^{12}C^{34}S$, $^{13}C^{32}S$ and ^{33}S nuclear quadrupole hyperfine structure of $^{12}C^{33}S$ were observed and measured. The analysis of the observed triplet corresponding to the ^{33}S nuclear quadrupole hyperfine structure of $J = 0 \rightarrow 1$ transition yields the rotational constant B_0 and quadrupole coupling constant eQq as 24293.32(0.02) MHz and 12.87(0.13) MHz, respectively with an assumed value of centrifugal distortion constant $D_J = 39.41$ kHz [11]. It has been noticed that no signal was observed below a discharge current of 100 mA for excited vibrational states. The measured and reported values of transition frequencies are compared in table 1. All the measured values have been reproduced within the quoted experimental uncertainty of measurement.

3.2 *Millimeterwave spectroscopy of fluorine cyanide (FCN)*

The millimeterwave spectra of fluorine cyanide and several of its isotopic species in which fluorine atom is attached to a triply bonded carbon atom have been reported by Sheridan and Tayler [13,14] who have obtained an r_s structure for this molecule. The infrared spectrum of FCN have been reported by Dodd and Little [15] who have also calculated force constants for this molecule. In ref. [14], FCN was prepared by passing the vapour of cyanuric trifluoride over a white hot platinum spiral. The millimeter- and submillimeterwave spectra of FCN were studied by Bogey *et al* [16] who have prepared FCN by the pyrolysis of $(FCN)_3$ in a graphite furnace. Tanaka *et al* [17] have used a DC discharge of pentafluorobenzonitrile to study the microwave spectrum of fluorocyanoacetylene

Table 1. Rotational transition frequencies (in MHz) of CS.

Species	v	Transition $J \to J'$	Transition $F \to F'$	Observed frequency	Reported frequency
$^{12}C^{32}S$	0	$0 \to 1$		48990.90	48990.978[a]
		$1 \to 2$		97980.85	97980.950[a]
	1	$0 \to 1$		48635.95	48635.977[a]
		$1 \to 2$		97270.90	97270.980[a]
	2	$0 \to 1$		48280.80	48280.887[a]
$^{12}C^{34}S$	0	$0 \to 1$		48206.92	48206.915[a]
		$1 \to 2$		96412.90	96412.940[a]
$^{13}C^{32}S$	0	$0 \to 1$		46247.55	46247.567[a]
		$1 \to 2$		92494.35	92494.308[a]
$^{12}C^{33}S$	0	$0 \to 1$	$3/2 \to 3/2$	48589.05	48589.074[b]
			$3/2 \to 5/2$	48585.80	48585.918[b]
			$3/2 \to 1/2$	48583.25	48583.290[b]

[a]Ref. [12], [b]ref. [11].

(FCCCN) where the signal of FCN was identified as an 'impurity' signal. We have used the newly constructed millimeterwave spectrometer to detect the rotational transitions of FCN, produced in the absorption cell by applying a DC discharge to a low pressure ($\sim$10 mTorr) flow of a few fluorobenzonitrile compounds. 2-fluoro, 3-fluoro, 2,3-difluoro and 2,6-difluorobenzonitrile compounds were used for this purpose. The discharge current was maintained at around 5 mA, which was found to be optimum for best signal intensity. Continuous DC discharge through a flow of the precursor gas was found to be essential to observe the signal unlike the case of FCCCN where a short duration (10 s) DC discharge was sufficient for the signals to remain for about 10 min [17].

Tayler and Sheridan [14] have reported the rotational and quadrupole coupling constants of FCN from an analysis of the rotational transitions. Using these constants the quadrupole hyperfine structure of $J = 2 \to 3$ transition was predicted which incidentally falls in the frequency range of our interest. We have observed and measured a triplet belonging to the $\Delta F = 0$ and ± 1 quadrupole hyperfine components of $J = 2 \to 3$ transition when a DC discharge was applied inside the cell through which a flow of fluorobenzonitrile compound has been maintained at low pressure. All fluorobenzonitrile compounds produced good signals of FCN. However, the signal intensity was found to be relatively better when 2,3- and 2,6-difluorobenzonitrile compounds were used as precursor gases. The observed transition frequencies along with some previously reported values were analysed using the usual expression for the frequency of a rotational transition of a linear polyatomic molecule with a single quadrupole nucleus [18].

$$\nu(J, F \to J+1, F') = 2B_0(J+1) - 4D_J(J+1)^3 + \nu_Q,$$

where ν_Q represents the contribution from quadrupole interaction. The rotational constant B_0, centrifugal distortion constant D_J and quadrupole coupling constant eQq of ^{14}N nucleus are fitted in a least squares fitting programme. The standard deviation of the overall fit comes out to be 0.05 MHz. Transition frequencies with their assignments and the derived parameters are listed in tables 2 and 3 respectively.

Table 2. Rotational transition frequencies (in MHz) of FCN in the ground vibrational state.

Transition		Frequency	
$J \rightarrow J'$	$F \rightarrow F'$	Observed	Obs. – Cal.
$0 \rightarrow 1$	$1 \rightarrow 1$	21107.71[a]	0.00
	$1 \rightarrow 2$	21108.50[a]	−0.02
	$1 \rightarrow 0$	21109.69[a]	−0.04
$1 \rightarrow 2$	$2 \rightarrow 2$ $0 \rightarrow 1$	42215.86[a]	0.05
	$1 \rightarrow 2$ $2 \rightarrow 3$	42216.64[a]	0.02
	$1 \rightarrow 1$	42217.94[a]	−0.02
$2 \rightarrow 3$	$3 \rightarrow 3$	63323.60[b]	−0.05
	$1 \rightarrow 2$ $2 \rightarrow 3$ $3 \rightarrow 4$	63324.50[b]	−0.02
	$2 \rightarrow 2$	63325.80[b]	0.06

[a]Ref. [14], [b]this work.

Table 3. Rotational constant, centrifugal distortion constant and ^{14}N nuclear quadrupole coupling constant ($\chi_{aa} = eQq$) of FCN in the ground vibrational state (estimated uncertainties are given in parentheses).

B_0 (MHz)	10554.207 (0.021)
D_J (kHz)	6.666 (0.685)
eQq (MHz)	−2.692 (0.051)
σ (MHz) (standard deviation)	0.049

4. Summary

The construction details of a millimeterwave spectrometer to study the rotational spectra of transient molecules in the gas phase have been presented. The performance of the spectrometer was checked with test samples, e.g., carbon monosulfide (CS) and fluorine cyanide (FCN) produced inside a free space absorption cell by applying a DC discharge through a low pressure flow of precursor gases. Signals of CS corresponding to the second and fourth harmonics of the fundamental klystron frequency were recorded side by side. The quadrupole hyperfine structures of ^{33}S and ^{14}N nucleus of ^{12}C^{33}S and ^{19}F^{12}C^{14}N have been resolved, measured and analysed. Bidirectional square wave was used as an efficient means of frequency modulation of the klystron frequency. Finally, it has been verified that the method of DC discharge inside an absorption cell can be used efficiently to generate transient molecules in the gas phase without affecting the detection system of the spectrometer.

Work is underway to extend the frequency range of investigation and to improve upon the sensitivity and resolution of the spectrometer.

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