Millimeter wave spectrum of ICN, a transient molecule of chemical and astrophysical interest

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Abstract. The discovery of many transient molecules in the interstellar space has evoked tremendous of research activity in the field of laboratory microwave and millimeter wave spectroscopy of transient species. We have used a recently assembled millimeter wave spectrometer to produce and study the ground state millimetre wave rotational spectrum of cyanogens iodide (ICN). ICN was produced using a DC discharge through a low pressure mixture of methyl iodide (CH₃I) and benzyl cyanide (C₆H₅CH₂CN) vapour. Iodine quadrupole hyperfine structure has been resolved, measured and analysed. Finally, internuclear distances of ICN have been determined and compared with the previously reported values.

1. Introduction:

The discovery of many transient molecules e.g., molecular ions, free radicals and other unstable species in the interstellar space by radio astronomers has evoked tremendous amount of research activity in the field of laboratory microwave and millimeter wave spectroscopy of transient species. Interstellar molecules having spectra in these frequency regions provide us with valuable information regarding the environment where these molecules exist. In general, the transient molecules are chemically active and it is very difficult to produce them in high concentrations in the laboratory. However, sustained efforts by several groups of dedicated laboratory spectroscopists around the world have made it possible to generate and study transient molecules in the laboratory. Dousmanis et al. [1] first observed several \( \Lambda \)-type doubling transitions of OH, a free radical, produced by a DC discharge through low pressure water vapor outside the cell. The lifetime of OH was estimated to be about 1/3 of a second and its concentration to be around 10% in the cell. About 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 O\(_2\) with OCS, H\(_2\)S and solid sulphur. The initial hesitation of making DC discharge inside the absorption cell was successfully overcome by R. C. Woods [4] who developed a free space absorption cell and showed for the first time that transient species could be produced inside the cell by a low pressure DC discharge through a mixture of precursor gases without affecting the detection system of the spectrometer. Dixon and Woods [5] later 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]. According to the latest information, more than 136 molecules have been identified.
by radio astronomers in the interstellar space [8] and one or more such species are being added to the list almost every year. The list of Ref. [8] includes some triatomic metallic cyanides and isocyanides e.g., MgCN, NaCN, MgNC, AlNC etc. However, halogen cyanides (XCN, where X=F, Cl, Br and I) have not yet been identified in the interstellar space.

In three recent communications, we have reported the analysis of the millimeter wave rotational spectra of some halogen cyanides e.g., fluorine cyanide (FCN) [9], chlorine cyanide (ClCN) [10] and bromine cyanide (BrCN) [11] produced by DC glow discharge technique. The nuclear quadrupole hyperfine structures arising out of the quadrupole nuclei $^{35}$Cl, $^{37}$Cl, $^{79}$Br and $^{81}$Br have been resolved, measured and analyzed resulting in the determination of very accurate rotational, centrifugal distortion and quadrupole coupling constants for these species. Finally, internuclear distances of CICN and BrCN have been determined. The remaining halogen cyanide in this group is iodine cyanide (ICN). The analysis of the first microwave spectrum of ICN was published as early as in 1947 [12] and subsequently T. Oka et.al [13], J. K. Tayler et.al. [14] and J. B. Simpson et.al [15] have reported the analysis of the microwave spectrum of ICN. However, in all the previous works, ICN was either procured commercially or prepared chemically.

In the present communication, we report the assignment and analysis of millimeter wave rotational transitions along with the iodine nuclear quadrupole hyperfine structure for each transition of ICN produced by DC glow discharge through a low pressure mixture of methyl iodide (CH$_3$I) and benzyl cyanide (C$_6$H$_5$CH$_2$CN). J – values from 8 to 14 are involved in this work covering the frequency range 50.0 – 99.0 GHz. Accurate values of the rotational, centrifugal distortion and quadrupole coupling constants were determined from a least-squares analysis of the observed data. Finally, using the parent and isotopic species data the internuclear distances I-C and C≡N have been determined and compared with the previous reported values.

2. Experimental details:
The spectrometer used in the present work is basically a 50 kHz source-modulated system combined with a free space glass discharge cell of 1.5 m in length and 10 cm in diameter. The cell is fitted with two Teflon lenses, which serve 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 top ends of the two tungsten wires have been used to apply DC voltage through a low pressure mixture of different precursor gases. A high voltage DC regulated power supply (6 KV, 1300 mA) procured from Glassman, Japan was used for this purpose. Using the DC discharge method, transient molecules of chemical and astrophysical interest 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 which enable us to distinguish paramagnetic lines from the lines of neutral species. An arrangement of flowing liquid nitrogen vapor from a pressurized liquid nitrogen vessel through a copper jacket surrounding the vessel has been made to cool the entire cell during continuous operation of the spectrometer. Cooling the cell quite often helps in enhancing the signal intensity. The cell is connected with a high vacuum pump at one end and to the sample holder section through a glass port on the other.

Klystrons and Gunn diodes followed by frequency doubler (Millitech model MUD-15-H23F0 and MUD-10-LF000) have been used as radiation sources. Millimeter-wave radiation was fed into the free space absorption cell by a waveguide horn and Teflon lens. A similar horn and lens arrangement was used to focus the millimeter-wave power onto the detector after propagating through the cell. The output frequencies of the klystrons and Gunn diodes were frequency modulated by a double square-
wave of 50 kHz [16] and the signal from the detectors (Millitech model DBT-15-RP000 and DXP-10-RPFW0) was amplified by a 100 kHz tuned preamplifier and detected by a phase-sensitive lock-in-amplifier in the 2f mode. The output of the lock-in-amplifier has been connected to an oscilloscope or a chart recorder for signal display. The signals could be stored on a computer disc for later use. The uncertainty in the frequency measurement has been estimated to be ± 0.15 MHz. Details of the spectrometer used have been described elsewhere [9].

Cyanogen iodide was produced inside the absorption cell by applying a DC glow discharge through a low pressure (~ 5-10 mTorr) mixture of Methyl Iodide (CH$_3$I) and Benzyl Cyanide (C$_6$H$_5$CH$_2$CN) vapor. The discharge current was maintained at around 5 mA. A continuous discharge was found to be essential for observing the signals. The signals vanished immediately after the discharge was switched off. This indicates the transient nature of the most important discharge product, ICN.

3. Rotational spectrum and analysis:
The ground state rotational spectrum including the quadrupole hyperfine structures of ICN for J = 8 to 14 transitions were predicted using the rotational and quadrupole coupling constants reported earlier [15]. Iodine having nuclear spin I=5/2, shows a characteristics six fold splitting of each rotational state. The $\Delta F = +1$ transitions resulted in two nearby strong triplets and corresponding $\Delta F = 0$ transitions showed relatively weak signals. As expected, the $\Delta F = -1$ transitions were predicted to be too weak to be observed by our spectrometer.

First of all, two nearby strong triplets corresponding to the $\Delta F= +1$ transitions were searched near the predicted frequencies and measured for all the J+1 $\rightarrow$ J transitions. Later on, a few moderately weak signals corresponding to $\Delta F=0$ components were also measured. The observed and assigned transition frequencies along with their respective quantum numbers are presented in Table – 1. The quadrupole hyperfine structure due to $^{14}$N nucleus was not resolved. The spectral recording of the $\Delta F= +1$ components of the quadrupole hyperfine structure of J = 15 $\rightarrow$ 14 transition is shown in Fig.1. It is to be noted here that a small splitting of the order of 100 kHz between the components F=29/2 $\rightarrow$ 27/2 and F=25/2 $\rightarrow$ 23/2 at 96756.1 MHz could not be resolved. Hence, both the components were assigned with the same frequency. The observed transition frequencies were analyzed using the following expression for the frequency of rotational transitions of a linear polyatomic molecule with a single quadrupole nucleus [17],

$$v (J+1,F' \leftrightarrow J, F) = 2B_0 (J+1) - 4 D_J (J+1)^3 - eQq \Delta Y(J, I, F)$$

where $B_0$, $D_J$ and $eQq$ are rotational, centrifugal distortion and quadrupole coupling constants respectively and $Y (J, I, F)$ is the Casimir function. All the transition frequencies reported in Table-1 were used to determine $B_0$, $D_J$ and $eQq$. The derived parameters are listed in Table-2 and compared with the previous reported values. The agreement between the two sets of values indicates that the assigned transition frequencies of Table-1 definitely belong to the discharge product ICN. The observed frequencies have been corrected to second order quadrupole terms for the determination of the quadrupole coupling constant $eQq$.

4. Molecular Structure:
The values of the ground state rotational constant $B_0$ of ICN and its isotopic species were used to calculate the internuclear distances. Kraitchman’s equation [18] was used to find out the center of mass to C and N atom distances. Reported literature values of the rotational constants of $^{13}$C and $^{15}$N species of ICN [15] were used in the calculation. Since iodine has no other isotopic species the center of mass to I atom distance was calculated using the first-moment equation: $\Sigma m_i z_i = 0$. Finally, internuclear distances were determined for I - C, C $\equiv$ N and I....N bonds. The effect of zero-point
vibration was neglected in these calculations. The average values of bond lengths obtained are as follows: I – C = 1.9944 Å, C≡N = 1.1585 Å, and I…N = 3.1529 Å which are quite comparable with the previously reported values of I – C = 1.9943 Å, C—N= 1.1584 Å and I….N = 3.1527 Å [19].

Table 1. Frequencies (MHz) of rotational transitions of ICN in the ground vibrational state (v=0).

| J' | J  | F' | F  | Observed   | Obs.– Calc. |
|----|----|----|----|------------|-------------|
| 9  | 8  | 23/2| 21/2| 58062.82  | 0.02        |
| 9  | 8  | 21/2| 21/2| 57664.70  | -0.01       |
| 9  | 8  | 21/2| 19/2| 58066.50  | 0.03        |
| 9  | 8  | 19/2| 19/2| 57939.50  | -0.03       |
| 9  | 8  | 19/2| 17/2| 58059.15  | 0.02        |
| 9  | 8  | 17/2| 17/2| 58137.35  | -0.04       |
| 9  | 8  | 17/2| 15/2| 58049.70  | -0.02       |
| 9  | 8  | 15/2| 15/2| 58274.57  | -0.06       |
| 9  | 8  | 15/2| 13/2| 58045.20  | -0.03       |
| 9  | 8  | 13/2| 13/2| 58364.90  | -0.09       |
| 11 | 10 | 27/2| 25/2| 70962.20  | 0.05        |
| 11 | 10 | 25/2| 23/2| 70964.70  | 0.00        |
| 11 | 10 | 23/2| 21/2| 70960.05  | 0.03        |
| 11 | 10 | 21/2| 19/2| 70953.80  | 0.01        |
| 11 | 10 | 19/2| 17/2| 70950.65  | -0.05       |
| 11 | 10 | 17/2| 15/2| 70954.30  | -0.05       |
| 13 | 12 | 31/2| 29/2| 83861.45  | 0.01        |
| 13 | 12 | 29/2| 27/2| 83863.40  | 0.09        |
| 13 | 12 | 27/2| 25/2| 83860.10  | 0.03        |
| 13 | 12 | 25/2| 23/2| 83855.70  | 0.06        |
| 13 | 12 | 23/2| 21/2| 83853.40  | 0.07        |
| 13 | 12 | 21/2| 19/2| 83855.90  | 0.00        |
| 13 | 12 | 29/2| 29/2| 83473.00  | 0.03        |
| 13 | 12 | 27/2| 27/2| 83718.80  | -0.01       |
| 13 | 12 | 25/2| 25/2| 83914.90  | 0.02        |
| 13 | 12 | 23/2| 23/2| 84068.70  | -0.01       |
| 13 | 12 | 21/2| 21/2| 84187.00  | 0.03        |
| 14 | 13 | 33/2| 31/2| 90310.90  | -0.04       |
| 14 | 13 | 31/2| 29/2| 90312.60  | 0.03        |
| 14 | 13 | 29/2| 27/2| 90309.80  | -0.01       |
| 14 | 13 | 27/2| 25/2| 90306.10  | 0.10        |
| 14 | 13 | 25/2| 23/2| 90303.95  | -0.03       |
| 14 | 13 | 23/2| 21/2| 90306.10  | -0.07       |
| 14 | 13 | 31/2| 31/2| 89924.10  | 0.00        |
| 14 | 13 | 29/2| 29/2| 90165.30  | -0.01       |
| 14 | 13 | 27/2| 27/2| 90360.80  | -0.01       |
| 14 | 13 | 25/2| 25/2| 90517.10  | 0.05        |
| 14 | 13 | 23/2| 23/2| 90639.80  | -0.01       |
| 15 | 14 | 35/2| 33/2| 96760.30  | 0.00        |
| 15 | 14 | 33/2| 31/2| 96761.70  | -0.03       |
| 15 | 14 | 31/2| 29/2| 96759.40  | 0.05        |
| 15 | 14 | 29/2| 27/2| 96756.10  | 0.06        |
| 15 | 14 | 27/2| 25/2| 96754.20  | -0.06       |
| 15 | 14 | 25/2| 23/2| 96756.10  | -0.05       |
| 15 | 14 | 33/2| 33/2| 96374.85  | -0.04       |
| 15 | 14 | 31/2| 31/2| 96612.00  | -0.09       |
| 15 | 14 | 29/2| 29/2| 96807.00  | -0.04       |
| 15 | 14 | 27/2| 27/2| 96965.30  | -0.02       |
| 15 | 14 | 25/2| 25/2| 97092.00  | 0.03        |
Table 2. Rotational constants, centrifugal distortion constants, and quadrupole coupling constants ($\chi_{aa} = eQq$) of ICN in the ground state along with the estimated uncertainties.

| Constants     | This work       | Ref. [15]       |
|---------------|-----------------|-----------------|
| $B_o$ (MHz)   | 3225.549(2)     | 3225.542(1)     |
| $D_j$ (kHz)   | 590.77(27)      | 589.0(5)        |
| $\chi_{aa}$ (I) (MHz) | -2420.85(9) | -2420.5(1) |

Figure 1. Quadrupole hyperfine structure of $\Delta F = +1$ component of $J = 15 \leftarrow 14$ transition.

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