

Infrared-radiofrequency double resonance spectrometer : an unique machine to probe excited vibrational states

R N Nandi^a, A K Bhattacharya and A I Jaman^{*}

Saha Institute of Nuclear Physics, Sector-1, Block-AF, Bidhannagar, Kolkata-700 064, India

E-mail : jaman@cmp.saha.ernet.in

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Abstract : The construction of an Infrared-Radiofrequency Double Resonance (IR-RF DR) spectrometer to study 'pure' nuclear quadrupole hyperfine spectra in the ground and excited vibrational state of a molecule in the gas phase is presented. An indigenously built CO₂ laser was used as the Infrared radiation source. The spectrometer has been used to observe 'pure' nuclear quadrupole hyperfine spectra of methyl iodide (CH₃I), a symmetric top molecule with a single quadrupole nucleus.

Keywords : Molecular spectroscopy, quadrupole hyperfine spectra, excited state.

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1. Introduction

In a particular vibrational state, microwave rotational spectral lines arise from transitions between two quantized rotational energy levels which obey Boltzmann's distribution law at thermal equilibrium and get splitted into different quadrupole hyperfine components in presence of a quadrupole nucleus (nuclear spin $> \frac{1}{2}$) in the molecule. The separation between different quadrupole sublevels, in general, falls in the radio frequency region of the electromagnetic spectrum.

Microwave rotational spectra and 'pure' nuclear quadrupole hyperfine spectra in the excited vibrational state of a molecule in the gas phase are difficult to observe due to the fact that the excited vibrational states are not sufficiently populated at ambient temperature because of the Boltzmann distribution law. However, the problem of insufficient population can be overcome by 'pumping' molecules from the ground to the desired excited vibrational state with a suitable laser radiation. Once the 'pumping' is achieved, the molecular sample can be irradiated with an appropriate microwave or radio frequency radiation depending upon the nature of interest and the spectro-

scopic studies can be conducted easily in the desired excited vibrational state. This technique is known as Infrared-Microwave (IR-MW) or Infrared-Radio Frequency Double Resonance (IR-RF DR) technique and has been pioneered and extensively used by Oka [1-4] for various studies of molecular properties in the excited vibrational states.

The intensity of radio frequency absorption spectrum is very small because of the low energy of radio frequency photons and due to the small population difference between the two levels. As a result, conventional radio frequency spectroscopic technique could not become a popular spectroscopic tool. In an IR-RF DR experiment, these difficulties have been overcome by detecting infrared laser radiation having larger photon energy rather than the RF radiation and by producing a non-Boltzmann distribution with an infrared laser 'pumping'.

In the present communication, the design and construction of an IR-RF DR spectrometer is presented. The spectrometer has been used to observe 'pure' nuclear quadrupole spectrum of gaseous methyl iodide (CH₃I) in its ground and excited vibrational state ν_6 .

^aCorresponding Author

^{*}Deceased

2. Experimental set-up

A block diagram of the experimental set-up for Infrared-Radiofrequency double resonance spectroscopy is shown in Figure 1. A coaxial rf cell (details shown in Figures 2(a)

tion, is chosen by rotating a plane grating. RF radiation obtained from a Frequency Synthesizer (Rohde-Schwarz Model SMG-B1, 100 kHz–1000 MHz) at a power level of -15 dBm was amplitude modulated at 10 kHz with the help

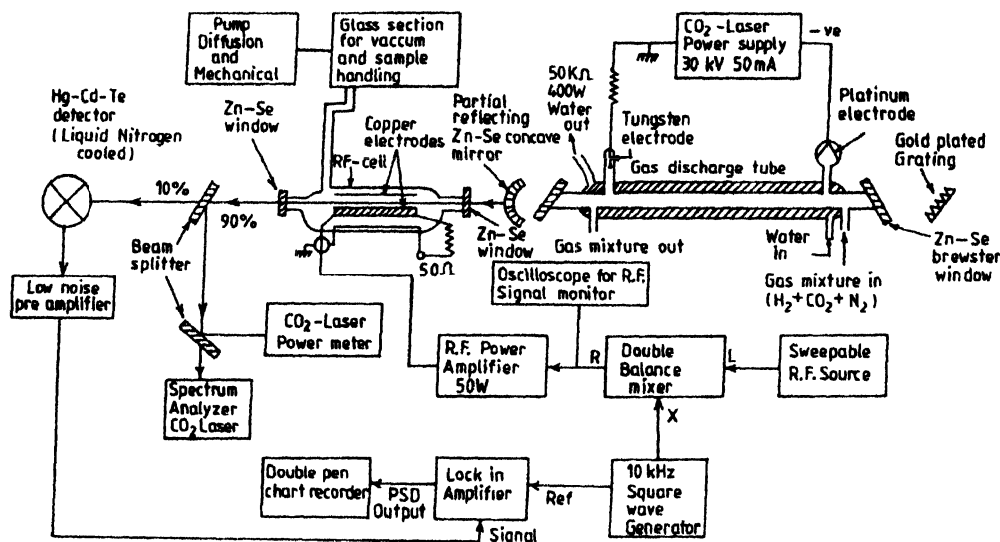


Fig. 1

Figure 1. Block diagram of Infrared-Radiofrequency Double Resonance Spectrometer

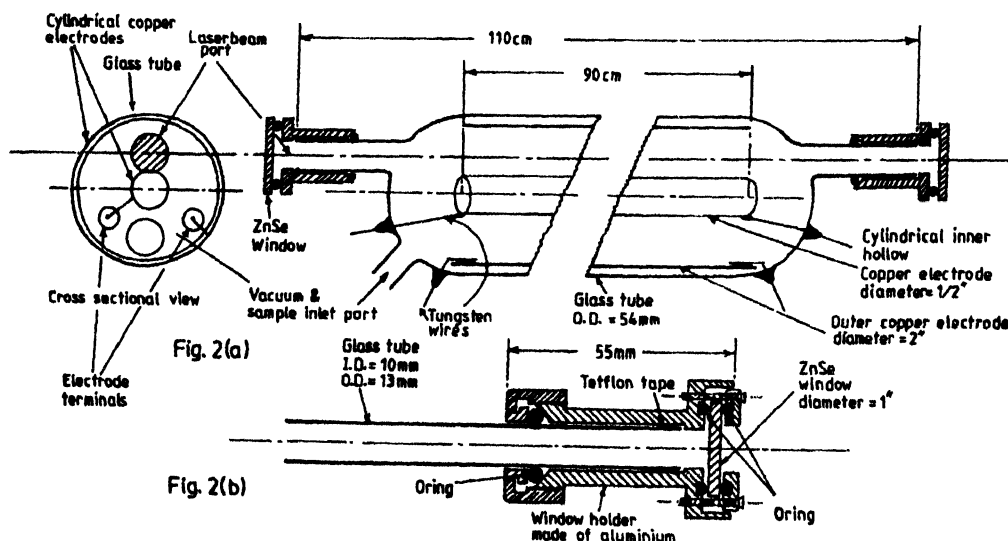


Fig. 2(a)

Fig. 2(b)

Figure 2 (a). Details of coaxial RF cell design. (b). Laser window holders for coaxial RF cell.

and 2(b)) containing the gaseous sample under investigation at low pressure is irradiated with an infrared laser radiation produced with an indigenously built CO₂ laser. The laser beam after passing through the cell falls on a crystal detector through a 10% transmission curved mirror. The infrared laser line, coincident with a particular vibration-rotation transition frequency of the molecular absorp-

tion of a double balance mixer (HP 10514A) and fed to a power amplifier (ENI 550L). The amplified RF radiation was subsequently fed to the absorption cell which was terminated to the ground through a 50 Ω resistor. The sample pressure was maintained at around 10–20 mTorr with the help of a combination of appropriate mechanical and diffusion pump. The laser output was monitored with a liquid nitro-

gen cooled Hg-Cd-Te detector (EG & G Judson, USA). In this experiment, the laser frequency was kept fixed and the RF radiation was scanned. When the RF frequency passes through a molecular absorption, the load characteristics of the gaseous sample changes and a sharp variation of the laser output power is observed as a double resonance signal. The detector output was accordingly modulated at 10 kHz, phase-sensitively detected by a lock-in-amplifier and recorded on a chart recorder.

returned to the ground through a ballast resistor of 50 KΩ/400 W rating. A Matheson (USA) flowmeter was used to maintain the flow of a mixture of CO₂, N₂ and He gases through the discharge tube. The discharge tube was connected to a mechanical pump. An approximate ratio of 1 : 1 : 4 was maintained for CO₂, N₂ and He through the flowmeter and was varied sometimes to achieve maximum laser power. The discharge tube was placed inside a

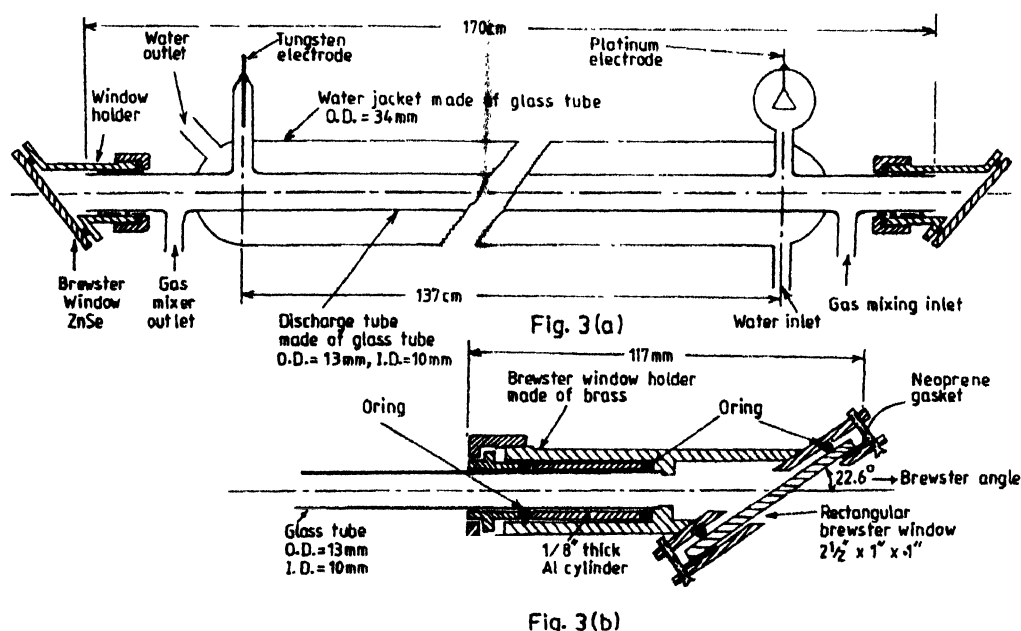


Figure 3 (a). Details of CO₂-laser gas discharge tube design. (b). Details of Brewster window holder design.

3. CO₂ laser construction : a brief description

A 1.7 meter long pyrex tube with an inner diameter of 10 mm and outer diameter of 13 mm has been used as the discharge tube (details shown in Figures 3(a) and 3(b)). The outer wall of the discharge tube is surrounded with a glass jacket for water-cooling. The two ends of the discharge tube are closed with rectangular Brewster windows which hold the gas mixture at desired pressure (7–10 Torr). The Brewster's windows are made of ZnSe which permits the transmission of infrared radiation of the CO₂ laser as well as the visible radiation of He-Ne laser. The visible radiation is used for the alignment of optical components. The D.C. discharge in the tube is maintained by applying a high negative voltage (~15 KV) at the cathode end. For this purpose, a high voltage D.C. regulated power supply (30 kV, 66 mA) procured from Glassman, Japan (Model LT) has been used. A platinum cone was used as the cathode and a tungsten wire as anode. The anode was

Febry-Perot cavity consisting of a curved mirror (10% transmission) and a grating separated by an approximate distance of 2 meters. The cavity length was kept fixed by using three pieces of Invar rods fixed on two triangular shaped metallic blocks. Two kinematic mounts have been used to place the partially transmitting mirror and the grating. The kinematic mount at the grating end can be adjusted for selecting a particular laser line of interest. In order to identify the actual laser line during lasing, a part of the laser radiation coming out of a partially transmitted mirror (10% transmission and 90% reflection) placed after the cell is extracted by a beam splitter and allowed to fall on a CO₂ spectrum analyser (Model 16-A, Optical Engineering, Lasercraft Inc., USA). From the calibrated display screen of the spectrum analyser the wavelength of the laser radiation can be obtained. Other part of the laser is fed to a CO₂ laser power meter (Sciencetech, model 37-4002) for measuring the laser power.

4. Nuclear quadrupole hyperfine structure of methyl iodide (CH₃I)

Methyl iodide is a symmetric top molecule where the rotational state in any particular vibrational state is denoted by the eigenstate $|JK\rangle$ where J is the rotational angular momentum and K is its projection along the molecular symmetry axis. In the CH₃I molecule, a hyperfine splitting occurs because of the interaction between the iodine nuclear quadrupole moment (nuclear spin = 5/2) and the electric field gradient produced by the electron cloud at the quadrupole nuclear site. Due to this interaction, J gets coupled with I to produce the resultant angular momentum F ($F = J + I$) which can take values from $|J - I|$ to $|J + I|$. The energy level diagram for vibration-rotation transition $16_6 \leftarrow 15_5$ of ν_6 , fundamental band of CH₃I is shown in Figure 4.

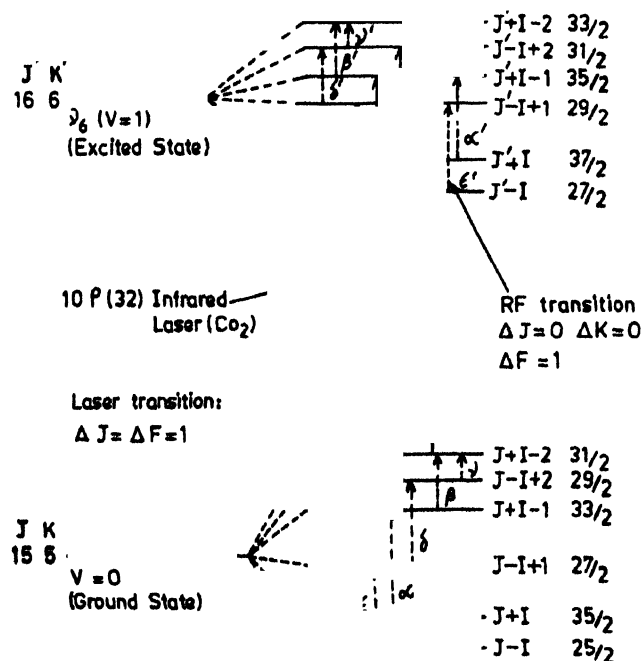


Figure 4. Energy level diagram for vibration-rotation transition $16_6 \leftarrow 15_5$ of ν_6 fundamental band of CH₃I.

The dipole selection rule $\Delta K = 0$, and $+$ \rightarrow $-$ for rotational transitions in a symmetric top molecule allow transitions with $\Delta J = 0$ and $\Delta F = 1$ between the hyperfine levels of rotational states with $K \neq 0$, because these states have a double parity. In Figure 4 the quadrupole splitting in the lower and upper states of an infrared transition are schematically shown. Five rf transitions are allowed in each state and are denoted by α , β , γ , δ , and ϵ in the ground state and α' , β' , γ' , δ' , and ϵ' in the excited state.

Since the hyperfine splitting has a similar pattern in the lower and upper state, the infrared transitions with $\Delta F = \Delta J$ are close in frequency which spans a frequency range comparable to the Doppler width of the methyl iodide vibrational transitions. Hence, the laser line can often pump all these transitions and as a result, all the five resonances are observed in both states in a double resonance experiment. Conversely, the $\Delta F \neq \Delta J$ infrared transitions have a longer spread in frequency and the laser has coincidence with only one or two of them. As a result, not all hyperfine levels are pumped and only a few rf resonances are observed in double resonance experiment. The nuclear quadrupole energy expression [5] for the iodine nucleus on the axis of symmetry is

$$W_Q(I, J, F) = eqQ [3K^2/J(J+1) - 1] Y(I, J, F) + E_Q^{(2)}(eqQ)^2/B,$$

where eqQ is the quadrupole coupling constant, $Y(I, J, F)$ is the Casimir function and $E_Q^{(2)}$ is the coefficient of second order perturbation contribution on the rotational energy levels and B is the rotational constant.

5. Performance of the spectrometer

The performance of the spectrometer described above has been checked with a test sample of methyl iodide. Methyl iodide has a number of normal vibrational frequencies. Its ν_6 vibrational mode coincides with the $10 \mu\text{m}$ region of the CO₂ laser. The 'pure' nuclear quadrupole resonances of gaseous CH₃I have been investigated in detail by Oka [2] using Infrared-radiofrequency double resonance spectroscopy. Therefore, precise values of quadrupole resonance frequencies are available in Ref. [2]. First of all, we looked for the double resonance signal $R(15_5)$, ν_6 ($V = 1$) \leftarrow 0 transition of methyl iodide. Here, the infrared transition connects the $J = 15$, $K = 5$ level of the ground state with the $J = 16$, $K = 6$ level of the excited vibrational state ν_6 . The $10P(32)$ line of the CO₂ laser matches this separation. The 'pure' quadrupole resonance signal of $F = 31/2 \leftarrow 29/2$ for the excited state ν_6 at 100.123 MHz [2] was attempted first. The laser was tuned to $10P(32)$. The sample pressure at the coaxial rf cell was kept around 15 mTorr. The laser power was set at around 1.5 W. Under this condition, the rf frequency was swept ± 4 MHz around 100.123 MHz. A strong double resonance signal was observed when the rf generator frequency passes through 100 MHz. The genuineness of the double resonance signal was checked by pumping out the sample gas from the absorption cell while recording a repetitive scan of the signal. A gradual decrease in signal intensity confirms that this is a genuine double resonance signal. The repetitive scan of the signal

is shown in Figure 5. After this double resonance signal was confirmed, many other double resonance signals e.g., $F = 29/2 \leftarrow 27/2$ ($\nu = 0$) at 114.72 MHz, $F = 31/2 \leftarrow 33/2$

region. It is to be mentioned here that we have been able to observe some more double resonance signals using 10P(4) laser line as 'pump' radiation which are not reported

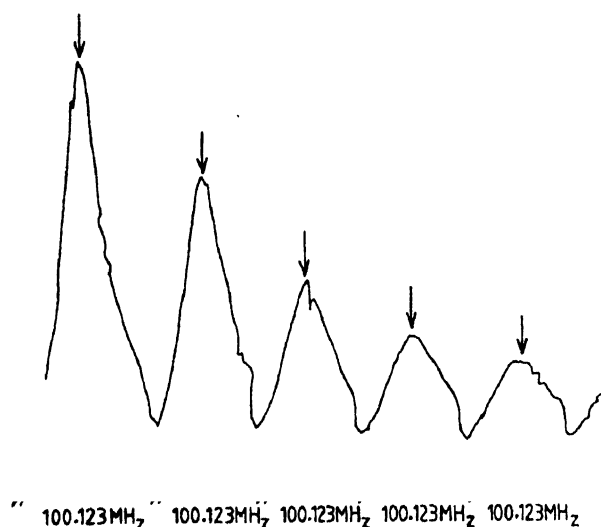


Figure 5. Repetitive scan of 100.123 MHz IR-RF DR signal ($F = 31/2 \leftarrow 29/2$, ν_6 ($\nu = 1$) $\leftarrow 0$) in pump-on condition.

($\nu = 0$) at 82.92 MHz and $F = 33/2 \leftarrow 35/2$ ($\nu = 1$ of ν_6 band) at 73.92 MHz were observed. These signals are shown in Figure 6. The same method of observation as stated earlier was followed. All the signals were verified by pumping out the sample from the absorption cell. As mentioned earlier that in principle, we should be able to

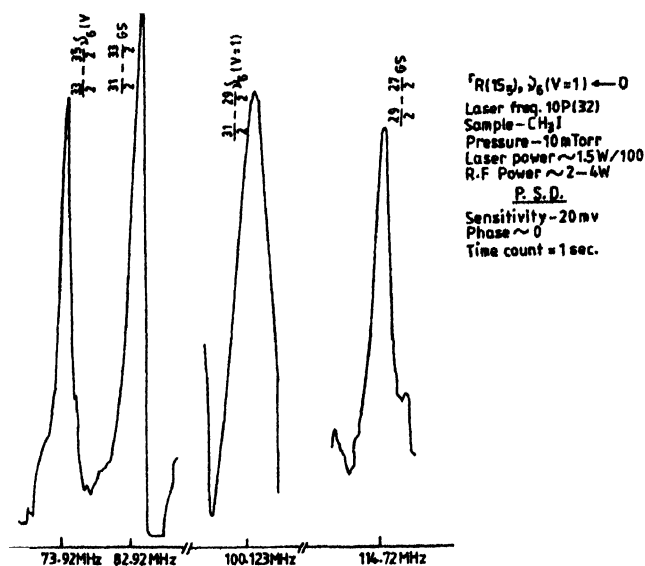


Figure 6. Other observed double resonance signals.

here. The observed 'pure' nuclear quadrupole resonance frequencies in the ground and ν_6 excited state are presented in Table 1. The quadrupole coupling constants eQq of CH_3I have been determined to be -1934.136 MHz and -1940.50 MHz for the ground and excited vibrational state respectively [2].

Table 1. 'Pure' quadrupole resonance frequencies (MHz) of CH_3I observed in the ground and ν_6 excited state.

Laser line	$^{12}\text{CH}_3\text{I}$ line	Ground state				ν_6 excited state					
		β	α'	β'	δ'						
10P(32) $^{12}\text{CO}_2$	$^1\text{R}(15)_2$, $\nu_6(\nu = 1) \leftarrow 0$	211.81	82.92	25.58 ^c	114.72	185.80 ^d	185.80 ^d	73.92	21.05 ^c	100.12	164.42

^cnot seen, ^dunresolved doublet.

observe 10 (5 each for ground and ν_6 excited vibrational state) double resonance signals with 10P(32) laser line. Hence, we looked for the remaining six double resonance signals for the sake of completeness. However, we have been able to observe three more double resonance signals e.g., at 164.4 MHz ($F = 29/2 \leftarrow 27/2$; $\nu = 1$ of ν_6 band), a strong signal at 185.8 MHz ($F = 27/2 \leftarrow 25/2$; $\nu = 0$ and $F = 35/2 \leftarrow 37/2$, $\nu = 1$ of ν_6 band coinciding with each other) and at 211.8 MHz ($F = 33/2 \leftarrow 35/2$; $\nu = 0$). The remaining two transitions ($F = 33/2 \leftarrow 35/2$; $\nu = 1$ of ν_6 band and $F = 31/2 \leftarrow 29/2$; $\nu = 0$) which are at 21.05 MHz and 25.586 MHz respectively could not be observed very clearly because of the RF source noise in this frequency

6. Conclusion

The details of the construction of an Infrared-Radiofrequency Double Resonance spectrometer has been presented. The spectrometer has been successfully tested to observe many double resonance signals for a number of vibration-rotation transitions of the test sample CH_3I . The genuineness of the signals were verified by pumping out the sample from the absorption cell which shows gradual decrease in intensity. This spectrometer has proved to be an excellent tool for probing molecular energy levels in the excited vibrational states. It is to be mentioned here that this method of observing 'pure' quadrupole resonance

frequencies of gaseous samples is applicable to any polar symmetric top molecule with a single quadrupole nucleus. Work is underway to incorporate some new devices to tune the laser over its entire gain-bandwidth curve so that the laser can be brought into resonance with some of the vibration-rotation transitions which are offset by 50 MHz or so.

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