CHAPTER 5

EXPERIMENTAL STUDY OF COLLISION BROADENING AND DETERMINATION OF DIPOLE MOMENT FOR $^{13}\text{CH}_3^{13}\text{C}^{15}\text{N}$ MOLECULE IN THE $^{n\nu}_8$ ($n = 0, 1, 2$) VIBRATIONALLY EXCITED STATES AT MICROWAVE FREQUENCIES

5.1 INTRODUCTION

The collision broadening of microwave spectral lines at low pressure is useful to provide information about the nature of the intermolecular forces. This field has been reviewed by Birnbaum$^1$, Krishnaji$^2$ and Rabitz$^3$. The high resolution of the microwave spectrometers and the extreme accuracy with which the absorption frequencies can be measured make it possible to determine the linewidth parameters very precisely$^4$. The double modulation microwave spectrometer used earlier$^5$, had a problem due to poor mode conversion in the rectangular to circular transitions before and after the cell combined with reflections from the mica windows. The standing waves in the system create difficulties in the measure of the linewidth parameters specially when absorption lines are weak. The standing waves are reduced by keeping the cell length to a minimum, and by observing higher harmonics of the Lorentzian resonance absorption profiles. There is usually a relative gain of the resonance power by observing higher harmonics of the power absorption compared to reflection power absorbed.

In this chapter, we have used the source modulation microwave spectrometer available$^5$ in the laboratory. The linewidth
parameters ($\Delta \nu/\Delta F$) of $^{13}\text{CH}_3^{13,15}\text{N}$ for $J = 1 \rightarrow 2$ rotational line in the ground, state $v_B = 1$ and $v_B = 2$ vibrational states at 300 °K were measured and are reported in this chapter. An experimental method is proposed for the first time for correction of modulation broadening when higher derivative than five Ref. (6), for Lorentzian spectral lineshape is used for weak rotational lines in the vibrationally excited states. Dipole moments of vibrationally excited species are determined using experimental linewidth parameters in the ground and in the excited vibrational state and the ground state value of the dipole moment (assumed to be the same as that for parent isotope $\text{CH}_3^{15}\text{N}$).

5.2 EXPERIMENTAL DETAILS OF SOURCE MODULATION MICROWAVE SPECTROMETER

Commercial sample of isotopically pure methyl cyanide ($^{13}\text{CH}_3^{13,15}\text{N}$) was procured from vendors (MSD Isotopes, Division of Merck-Frost, Canada Inc. Montreal, Quebec Canada). The sample is frozen under vacuum conditions and any excess gases pumped away via a cold trapped diffusion pump system in the standard way. Each sample is then stored in evacuated reservoirs until such time as needed.

The block diagram of double modulation microwave spectrometer with cell of length 121.92 m and diameter 0.016 m is shown in Fig. 5.1, with the major components. The Klystron output frequency modulated by a slow saw tooth voltage from the oscilloscope and a small amplitude audio frequency sinewave is propagated through the
Fig. 51 Block diagram of the source modulation line width spectrometer used in this investigation.
gas contained in the cell. The modulation frequency \( f \) was set to \( (f/n) \), \( f = 43.32 \text{ KHz} \), \( n = 8 \) to get eighth derivative of the line profile and was detected at 43.32 KHz. Each spectral profile and a set of markers generated as "beat" notes between the Klysteron frequency and a frequency standard system with the set of markers appear on one channel of a dual trace recorder and the spectral profile derivative (the 8th derivative was used in this work) appears on the other channel.

Frequency standardization and reference is achieved by using a General Radio Standard model 1112 A, B Phase locked to a Hewlett-Packard 105 A/B quartz oscillator, good to 1 part in 10\(^{10}\).

The gas used under investigation is admitted into the absorption cell at different pressures in the range 0.3 mTorr-10mTorr. Pressure measurements were made using a MKS Barytron model 170 M, which was factory calibrated and checked with a Standardized Mclead gauge. Absolute pressure measurements are assumed to be better than 0.5 percent, relative pressure measurements better than 0.1 percent. From the chart recorder trace of 8th derivative of the absorption profile at various pressures, half width at half power points are measured by measuring position of each maximum \( \nu \) of intensity from the centre frequency \( \nu_0 \). The ratio of \( \nu \sim \nu_0 \) to \( n \)-th root of \( [d^n I(\nu)/d(\nu \sim \nu_0)^n] = 0 \) for Lorentzian line shape of intensity \( I(\nu) \) was used as the half width \( \delta \nu \) at half power points. The average value \( <\delta \nu> \) obtained from various maxima position was taken. The eighth derivative gave us good signal to noise ratio when large modulation amplitudes were used.
The observed half width at half power points ($\delta \nu$) was then corrected for modulation, Doppler, cell length and wall broadening. After all corrections were applied the true half width ($\Delta \nu$) at half power points was obtained. A linear-least square routine was employed to find the best fit straight line for the plot of $\Delta \nu$ versus pressure. The slope of this line was taken to be the linewidth parameter ($\Delta \nu/\Delta P$).

5.3 THEORETICAL DETAILS FOR ANALYSIS OF EXPERIMENTAL DATA

Experimental studies of the shapes of microwave spectral lines in gases at low pressure were reported by Netterfield$^6$ and Johri and Srivastava$^7$. A method which might be used to eliminate the effects of the base line in the linewidth ($\Delta \nu$) measurements may be achieved by displaying higher derivative of the absorption profile by detecting at $f$ KHz and modulating at $\frac{f}{n}$ KHz. The intensity distribution for the Lorentzian lineshape at any frequency $\nu$ in a broad line is given by$^6,7$

$$I(\nu) = \frac{\Delta \nu}{(\nu - \nu_0 + \delta \nu_0)^2 + (\Delta \nu)^2}$$ (5.1)

where $\nu_0$ is the centre frequency of the line, $\delta \nu_0$ is the frequency shift, $\Delta \nu$ is the linewidth. Ignoring $\delta \nu_0$ and letting $\nu - \nu_0 = \chi$

$$I(\nu) = \frac{\Delta \nu}{\chi^2 + (\Delta \nu)^2}$$ (5.2)

By slowly sweeping the Klysteron frequency across the spectral line, the amplitude of the harmonic outputs are found to vary approximately as the derivative of the line which has the Lorentzian shape. The $n$-th differentiation of eqn. (5.2) with
respect to \( x \) gives

\[
\frac{d^n I(\nu)}{dx^n} = (-1)^n \frac{n!}{(\Delta \nu)^{n-1}} \sin^{n+1} \left( \sin(n+1) \phi \right)
\]

where \( \phi = \cot^{-1} \left( \frac{x}{\Delta \nu} \right) \) \[(5.3)\]

For the maxima positions, one needs to evaluate \( \frac{d^n I(\nu)}{dx^n} \)

\( = 0 \) and the respective roots of \( (x/\Delta \nu) \) are obtained. The separation of the maxima on the positive frequency side from the centre frequency for eighth derivative of Lorentzian line are 0.0, 0.3249, 0.7265, 1.3764 and 3.0777 for \( n = 1, 2, 3, 4, 5 \) respectively. The ratio \( (\nu - \nu_0)/n\text{-th root} \) was used to determine half width at half power points.

The lineshape displayed is not the true eighth derivative of a lorentz profile due to molecular collisions, but also has contribution from modulation, Doppler, cell length and wall collision broadening. The analytical expressions available in the literature are valid with some limitations. One of the important corrections is due to the modulation broadening for which the analytical expression for 8-th derivative is not available in the literature. Moreover, the signal to noise ratio of the detecting system is decreased as pressure is increased, which can be enhanced either by increasing the power or the modulation amplitude \((f')\). If modulation amplitude is increased large modulation broadening may be speculated. For this purpose an experimental method is proposed in this work to make corrections in the observed half width \((\delta \nu)\) for modulation broadening.
If data of $\delta v$ and $f'$ are available at fixed pressure, and linear relationship between $\delta v$ and $(f'/\delta v)^2$ is assumed we get

$$\delta v = m \left( \frac{f'}{\delta v} \right)^2 + C$$

(5.4)

where $m$ is the slope of the straight line plot of $\delta v$ versus $(f'/\delta v)^2$. The intercept $C$ includes the linewidth ($\Delta v$) and the correction term $[(f/n)/\Delta v]^2/2$ due to the modulation frequency ($f$). Therefore $\Delta v$ can be derived from the following equation

$$\Delta v = \delta v - m \left( \frac{f'}{\delta v} \right)^2 - \frac{1}{2} \left( \frac{f/n}{\delta v} \right)^2$$

(5.5)

$f'$ can be measured from the splitting of the marker and is called Klystron excursion frequency.

5.4 DETERMINATION OF DIPOLE MOMENT IN THE EXCITED STATE FROM COLLISION BROADENING

The dipole moment ($\mu_v$) for the vibrationally excited species can be estimated using the method presented by Ware et al.\(^5\), which gives

$$\mu_v \approx \mu_0 \left( \frac{\Delta v/\Delta P}{\Delta v/\Delta P}_{v=0} \right)_{v=v}$$

(5.6)

where $\mu_0$ is the ground state value of the dipole moment. Eqn. (5.6) is based on the assumption that only dipole-dipole interactions are dominant and also the changes in the transition energies, relative velocity etc. When the molecule goes from the ground to the excited vibrational states, are ignored. The measured linewidth parameters in ground and excited vibrational state along with available value of dipole moment in the ground vibrational state are required to determine dipole moment $\mu_v$. 
5.5 RESULTS AND DISCUSSIONS

An eighth derivative profile of rotational transition in ν₈ = 1 vibrational state of $^{13}$CH$_3^{13}$C$^{15}$N molecule at 2.9 and 5.5 mTorr pressures and modulation amplitudes $f' = 1.30$ and 1.32 MHz, measured frequency 34691.382 MHz are shown in Fig. (5.2). The effect of pressure on line widths is shown in Figure (5.2). The marker interval in Fig. (5.2) is 3 MHz. The plot of δν versus $(f'/δν)^2$ for the correction of the modulation broadening at fixed pressure 2.5 mTorr and for the ground vibrational state is given in Fig. (5.3). The slope of the straight line in Fig. 5.3 is $m = -0.0132$ MHz. Figs. (5.4), (5.5) and (5.6) are the plots of linewidth versus pressure for ν₈ = 0, ν₈ = 1 and ν₈ = 2 at 34623.419, 34691.382 and 34817.828 MHz respectively. The experimental results of linewidth parameters and dipole moment for the ground and excited vibrational states of $^{13}$CH$_3^{13}$C$^{15}$N molecule are given in Table 5.1.

The Doppler broadening was estimated using the procedures of Parsons and Roberts$^8$ and Townes and Schallow$^9$. This correction is less than 25 KHz. The contributions due to cell length, wall collisions and correction term $[(f/n)/6ν]^2$ due to modulation frequency (f) were insignificant for $^{13}$CH$_3^{13}$C$^{15}$N and for the rotational lines considered. The correction due to modulation broadening corresponding to the term $M (f'/δν)^2$ gives linewidth parameter 14.9% smaller than that without correction for ν₈ = 0. However for ν₈ = 1 and ν₈ = 2 the linewidth parameters are
Fig. 5.2. Scan of eighth derivatives with frequency markers for the measurement of linewidth at different pressures (A) 5.9 mTorr (B) 55 mTorr
Fig. 5.3. Plot of observed half width at half power points ($\delta_y$) versus ($4'/\delta_y$) for the correction of the modulation broadening at 25 mTorr and for $\gamma_B = 0$. 

Observed half width at half power points (kHz)
Fig. 5.4. Line width versus pressure for $J=1 \rightarrow 2, K=l=0$ rotational transition of the ground vibrational state of $^{13}\text{CH}_3^{13,15}\text{N}$. Measured frequency $34623.419$ MHz.
Fig. 5.5. Line width versus pressure for \( J=1 \rightarrow 2, K=1 \rightarrow -1 \) rotational transition of the \( v_8 = 1 \) vibrational excited state of \( ^{13}\text{CH}_3^{13}\text{C}^{15}\text{N} \). Measured frequency 34691.382 MHz.
Fig. 5.6. Line width versus pressure for $J=1 \rightarrow 2, K=-1, l=2$ rotational transition of the $v_8=1$ vibrational excited state of $^{13}{\text{CH}}_3{\text{C}}^{15}{\text{N}}$. Measure frequency 34817.828 MHz.
increases by 4.7% and 3.4% respectively, when corrections are applied.

The scattering of the data in figures 5.4, 5.5 and 5.6 is due to accumulated errors results from pressure and frequency measurements, errors in modulation locating the turning points for Spectral profile and other corrections etc. In the case of $v_B = 0$ part of the uncertainty may be attributed to the composite effect of frequencies $34623.419$ and $34622.802$ MHz. The overall uncertainty lies in the range 5 to 20 percent depending upon the intensity of the absorption line. Stronger ones were measured more accurately.

An examination of Table 5.1 shows that the dipole moments for the vibrational state $v_B = 1$ and $v_B = 2$ of $\text{CH}_3\text{C}^{15}\text{N}$ molecule are smaller than the ground state value 3.92 D (Ref. 10) which is assumed to be the same as that for parent isotope (CH$_3$C$^{15}$N). The change in the dipole moment for the $v_B = 1$ is 36.5 percent and that for $v_B = 2$ is 28.1 percent, these variations in the dipole moment values are rather large as compared to those determined by Messer and Roberts$^{10}$ for parent isotope, (CH$_3$C$^{15}$N) in the $v_B = 1$ using static stark effect for $JK = 1, 0 \rightarrow 2,0$ rotational line. But such changes were also found by Ware et al$^{5}$ for propyne molecule. Any rigorous formulation including the effects ignored in eqn. (5.6) may lead to better results.

Theoretical calculations of the linewidth parameters using existing models$^{11-13}$ to compare with the experimental ones have not been attempted as these models did not explain the observed
TABLE 5.1 Experimental Results of Linewidth Parameters and Dipole Moments of $^{13}\text{CH}_3^{15}\text{C}_2\text{N}$ molecule for ground and excited vibrational states for $\Delta J = 1 \rightarrow 2$.

<table>
<thead>
<tr>
<th>Rotational Level and Vibrational State</th>
<th>Component frequency (MHz)</th>
<th>Linewidth Parameter $\Gamma_1$ (MHz Torr)</th>
<th>Dipole Moment $\mu(D)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$J = 1, K = 0, \ell = 0$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\nu_B = 0$</td>
<td>34623.419</td>
<td>38.44</td>
<td>3.92*</td>
</tr>
<tr>
<td>$J = 1, K = 1, \ell = 0$</td>
<td>34622.802</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$\nu_B = 0$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$J = 1, K = 1, \ell = -1$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\nu_B = 1$</td>
<td>34691.382</td>
<td>24.40</td>
<td>2.49</td>
</tr>
<tr>
<td>$J = 1, K = -1, \ell = 2$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\nu_B = 2$</td>
<td>34817.828</td>
<td>27.62</td>
<td>2.82</td>
</tr>
</tbody>
</table>

* Ref. 10
linewidth parameters in the case of parent isotope \( \text{CH}_3\text{C}^{15}\text{N} \) reported earlier by Messer and Roberts\(^{14}\). There is need of formulating a model to explain the discrepancies observed.\(^{14}\)
REFERENCES