CHAPTER V

CONCLUSION

From the work included in this thesis following conclusions are made.

In the comparative study of interpolation schemes in the treatment of collisional transfer of rotational energy, it has been found in the self broadening of OCS considering dipole-dipole, dipole-quadrupole, quadrupole-dipole, quadrupole-quadrupole and dispersion interactions. The line width parameter calculated by using the Johri and Srivastava function in the transition J=1→2 line for $^{3}H_{1} OCS \approx 4.5 \text{ D} \bar{A}$ is the same as obtained by Prakash and Boggs using the Anderson's second approximation for $^{3}H_{1} OCS = 0.0 \text{ D} \bar{A}$. However, Murphy-Boggs theory gives $(\Delta \nu / \nu) = 6.08 \text{ MHz/Torr}$ for $^{3}H_{1} OCS = 4.5 \text{ D} \bar{A}$. The interruption function used here gives nearly 15% lower value of the quadrupole moment than the Murphy Boggs theory. The function formulated by Johri and Srivastava explains the observed width and the J-dependence better than the Murphy Boggs theory. Furthermore it includes the elastic collision in the framework of Anderson's theory.

From the study of temperature dependence and the state dependence, it is concluded that the
function formulated by Johri and Srivastava$^{30}$ gives smaller line width parameter than Mehrotra and Boggs$^{38}$ and the results obtained are closer to the experimental values$^{269,270}$. It is also found from the temperature variation study that as the temperature increases at the particular J-state, the deviation from the measured values decreases. The linewidth parameter decreases as the temperature increases. It is worth mentioning that all the interactions are to be included in the theoretical values to make the agreement close to the temperature variation of the measured line width.

From the study of consideration of phase shift effect in rotational transition in microwave region, it is concluded that the contribution of elastic collisions at microwave frequency is not negligible as assumed in the Murphy Boggs theory$^{22}$. The consideration of elastic collisions in addition to inelastic collisions in the collision interruption function formulated by Johri and Srivastava$^{30}$ is justified by the present calculations. Such a comparison has been done for the first time. The observed pressure shift$^{32,269}$ also favors the consideration of elastic collisions. A comparison of the contribution of elastic collision under the recent formulation of Mehrotra and Boggs$^{38}$ due to complex nature
of collision interruption function suggested in the Murphy Boggs theory\textsuperscript{22} with the contribution of elastic collisions considered by Johri and Srivastava reveals that the collision interruption function formulated by Johri and Srivastava\textsuperscript{28,30} is quite good to explain the observed widths. As $\cos \varphi \approx 1$, the Mehrotra and Boggs theory\textsuperscript{38} is expected to yield the same line width parameters as obtained by using Murphy Boggs theory\textsuperscript{22}. However, Mehrotra and Boggs theory\textsuperscript{38} may be useful for the line shift calculations. Till some quantum mechanical treatment to handle larger molecular systems and the non perturbative approach are put in the computational form, the function formulated by Johri and Srivastava\textsuperscript{30} will be used profitably in the calculation of collision cross section in the rotational energy transfer.

For pure rotation and under the assumption of Murphy Boggs theory\textsuperscript{22} a new alternative collision interruption function (eqn. 3.55) proposed in this thesis is different from the Murphy Boggs\textsuperscript{22} collision interruption function. It is better form of the function as it does not assume that the line width parameter arises due to the contribution of individual levels as considered by Murphy Boggs theory. Also total collision interruption function
is considered in the framework of Anderson's theory. Using this new function the calculated line width parameter are in reasonable agreement with observed values and may brought closer to the experimental line width parameters while including the other interactions. In addition to the dominant dispersion forces, except in OCS J=2→3 line perturbed by carbon tetrachloride. The reason for large discrepancy in OCS-CCl₄ may be partially due to non-zero value of dipole moment of CCl₄ in the excited vibrational state as observed by Ozier and Venkateshwarloo²⁶,²⁷.

From the study of line width parameters considering dipole-dipole interaction for self broadening of rotational absorption lines of linear molecule, it is shown that in self broadening of ICN J=3→4, where both functions formulated by Murphy and Boggs²² and Johri and Srivastava³⁰ give line width parameter larger than the observed values. However, by including other interactions, the calculated line width parameters brought closer to the measured line width parameters. The large discrepancies between the calculated and the measured linewidth parameters i.e. 42.2%, 43.2% in ICl J=3→4 and 47.5%, in TICl J=3→4 are due to errors in the measurements. It is concluded that inspite of large errors in the measurement, the measured values provide a test.
of the Johri and Srivastava\textsuperscript{30} function as applied to linear molecules considering only the dipole-dipole interactions.

By fitting the measured microwave linewidth to the theoretically calculated line width using Johri and Srivastava\textsuperscript{30} function, the quadrupole moments obtained from \( \text{Cl}_3\text{Br} \) and \( \text{C}_2\text{H}_4\text{O} \) (where \( x = \text{H}_2, \text{O}_2, \text{N}_2 \) and \( \text{CO}_2 \)) collisions are in agreement with literature values \( 139, 274, 279, 292, 298 \). In the calculations of linewidth parameters only dominant dipole-quadrupole interactions are considered, therefore, it is concluded that the linewidth data gives only the upper limiting value of the molecular quadrupole moment if all the molecular interactions are not included.

From the dielectric relaxation studies in liquids it is found that the dielectric data can be analysed by various representations like Gopala Krishna\textsuperscript{447}, Hiigasi\textsuperscript{446}, Cole-Cole arc plot and Eyring rate process with limitations and assumptions inherited in these formulations. However, for dilute solutions it is found that the new alternative formulation used in this thesis may interpret dielectric data well. This method gives dipole moment different from Gopala Krishna\textsuperscript{447} method. It is better in respect of using slope of
permittivity versus concentration in the calculation of dipole moment. The importance of using slopes has been mentioned earlier by Franklin et al.\textsuperscript{\textcopyright 440}. It is also concluded that the evaluation of the thermodynamical parameters are important to elucidate the mechanism of dipole rotation accompanying the dielectric relaxation phenomenon in polar liquids.

The $X$-band bench used for the measurement of permittivity and dielectric loss, has been tested using monochlorobenzene and benzophenon in benzene solution. It gives permittivity and dielectric loss in agreement with the values quoted in the literature with in the experimental uncertainty of about 5\%.