

# Some theoretical aspects of dielectric absorption and dispersion in polar gases and liquids

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Two main themes in the theory of dielectric relaxation are pursued. In one, present methods of band shape theory for a gas are refined and applied to ammonia inversion bands and to the rotation bands for symmetric top molecules. In the other, we include absorber-bath molecule correlation effects for the problem of dielectric relaxation in liquids. It is also shown how correlation effects between absorber and bath molecules enter the equations of motion for the electric dipole moment for ammonia gas.

The first theme directs particular attention to understanding the collapse of resonant band shapes with increasing pressures to nonresonant band shapes. A mechanism which predicts a possible secondary dispersion region for the  $\text{NH}_3$  and  $\text{ND}_3$  nonresonant spectra is identified using a refinement of Ben-Reuven's classical analogue [1, 2, 3]. Some indirect but inconclusive positive evidence is presented for  $\text{ND}_3$  [11, 12]. This classical result is also obtained with the semiclassical model presented in Chapter IV [9]. Further, the mathematical similarity of the rotation band shape theory for symmetric tops to the theory for  $\text{NH}_3$  and  $\text{ND}_3$  inversion bands is explored in a comparative study in Chapter III. A general approach which picks out the most dominant physical processes determining rotation band shapes is described. A detailed analysis of the  $J$ -diffusion model is given within this context [5].

Our second theme consists of separate parts, one for polar liquids and

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one for  $\text{NH}_3$  and  $\text{ND}_3$  gas inversion bands. In liquids, the effect of correlations arising from strongly hindering angular dependent inter-molecular forces is included phenomenologically by generalizing the angular brownian motion model for the electric dipole moment [4]. This is achieved by a large number of statistically interdependent reorientation events [8]. The end prediction is a distribution of relaxation times and/or multiple dispersion regions. Most likely applications are with associative liquids and some limited data on *n*-propanol have permitted a comparison of dielectric and ultrasonic relaxation times. The indication is that structural relaxation times are of the same order but smaller than the characteristic period for reorientation perturbations suggesting that structural relaxation is a rate determining process for dielectric relaxation.

Absorber-bath molecule correlations in  $\text{NH}_3$  and  $\text{ND}_3$  mixtures with foreign gases lead to several new collision cross-sections of spectral significance [9]. Ben-Reuven's two coupled equations for the dipole auto-correlation function are subsequently generalized to three equations. The corrections to the spectral shape function have yet to be looked for experimentally. It is shown that the most decisive test is to look at low pressures for an additional excess residual absorption line of zero resonant frequency [10].

In  $\text{NH}_3$  and  $\text{ND}_3$  pure gases, similar corrections to Ben-Reuven's theory exist but by way of two coupled dipole moment equations generalizing to 15 equations. This generalization has permitted a detailed comparison of the Fano Liouville formalism for the impact model with the pioneering theory of Margenau [6, 7], which is concerned with the idealisation of two stationary molecules interacting via dipole-dipole forces. A comparison of  $\text{NH}_3$  band shape and resonant line width data has indicated a significant deviation from the Ben-Reuven formula [9]. In its simplest form, the adjusted theory introduces a new cross-section which gives satisfactory agreement with experiment. For dipole-dipole forces, this cross-section is zero for straight line classical collision trajectories but can be nonzero for more realistic collision paths. Thus its value is more sensitive to the details of the collision process than, for instance, the half width.

## References

- [1] A. Ben-Reuven, "Transition from resonant to nonresonant line shape in microwave absorption", *Phys. Rev. Lett.* **14** (1965), 349-351.
- [2] A. Ben-Reuven, "Impact broadening of microwave spectra", *Phys. Rev.* **145** (1966), 7-22.
- [3] A. Ben-Reuven, "The meaning of collision broadening of spectral lines: the classical-oscillator analog", *Adv. Atom. Mol. Phys.* **5** (1969), 201-235.
- [4] P. Debye, *Polar molecules* (Dover, New York, 1929; reprinted, 1954).
- [5] R.G. Gordon, "On the rotational diffusion of molecules", *J. Chem. Phys.* **44** (1966), 1830-1836.
- [6] Henry Margenau, "Pressure broadening in the inversion spectrum of ammonia", *Phys. Rev.* **76** (1949), 121-124.
- [7] H. Margenau, "Inversion frequency of ammonia and molecular interaction", *Phys. Rev.* **76** (1949), 1423-1429.
- [8] D.R.A. McMahon, "Hindering and memory effects on the distribution of relaxation times in dielectric theory. I. Secondary dispersion regions in *n*-propanol", *J. Chem. Phys.* **62** (1975), 2880-2889.
- [9] D.R.A. McMahon, "On the inversion spectra of  $\text{NH}_3$  and  $\text{ND}_3$ ", submitted.
- [10] D.R.A. McMahon, "The  $\text{NH}_3$  and  $\text{ND}_3$  inversion spectra - the effect of dipole orientating collisions", in preparation.
- [11] D.R.A. McMahon and I.L. McLaughlin, "Classical theory of the dielectric loss for  $\text{NH}_3$  and  $\text{ND}_3$ ", *Phys. Lett.* **45A** (1973), 343-344.
- [12] D.R.A. McMahon and Ian L. McLaughlin, "On the classical microwave and infrared pressure broadening theory for ammonia", *J. Chem. Phys.* **60** (1974), 1966-1975.