

# METHODS OF Experimental Physics

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## SPECTROSCOPY

### 1.1.6. The Radio Frequency Region

The discovery of electrically produced electromagnetic waves by H. Hertz in 1887 and the study of their properties in terms of Clerk Maxwell's theory are parts of a familiar story. With the development of the thermionic vacuum tube, it became possible to use these waves in various systems of communication—and, incidentally, to employ them in a variety of ways in spectroscopy.

One of the earliest applications was in the determination of dielectric constants. It was found<sup>35</sup> in the case of polar molecules that the dielectric constant for very low frequencies was considerably higher than that for much higher frequencies; this was attributed to the inability of the polar molecules to follow the electric field at extremely high frequencies so far as orientation is concerned. At very low frequencies, measured polarization included effects due to both molecular orientation and molecular distortion, whereas at extremely high frequencies, the measured polarization is due to molecular distortion alone.<sup>36</sup> The dividing line between the two takes place at a frequency  $\nu$  defined by the equation  $\nu\tau = 1$ , where  $\tau$  is called the dielectric relaxation time.

These effects are associated with an anomalous dispersion that occurs in the radio frequency region in the case of many liquids<sup>37</sup>; the energy dissipation as reflected in the imaginary part of the dielectric constant represents a direct conversion of electromagnetic energy to the thermal energy associated with random motion of the molecules in the fields of their neighbors. It is thus related directly to viscosity effects; in the case

<sup>32</sup> J. Strong and G. A. Vanasse, *J. Phys. Radium* **19**, 192 (1958).

<sup>33</sup> J. Strong and G. A. Vanasse, *J. Opt. Soc. Amer.* **50**, 113 (1960).

<sup>34</sup> P. L. Richards, *J. Opt. Soc. Amer.* **54**, 1474 (1964).

<sup>35</sup> P. Drude, *Z. Phys. Chem.* **23**, 267 (1897).

<sup>36</sup> P. Debye, *Berichte* **15**, 777 (1913).

<sup>37</sup> P. Debye, "Polar Molecules." Chemical Catalogue Co., New York, 1929.

of solids, other related phenomena are involved. This type of absorption is called *Debye absorption*; the absorption line shape is quite different from that of other absorption lines.

Following the discovery of nuclear magnetic resonance (NMR) by Bloch and Purcell, special radio frequency techniques have been developed for the study of the phenomena involved.<sup>†</sup> When a sample containing a given type of nucleus with nonzero spin is placed in a strong magnetic field, the degeneracy involving the spatial quantum number is removed. The frequency separation of the resulting energy levels is related to the Larmor precessional frequency of the nucleus in the strong external field; transitions between these levels can be observed in absorption. In the case of liquids with low viscosity, the resulting lines are exceedingly narrow and are split by various characteristic molecular effects; true molecular splittings as low as a few Hz have been observed. Nuclear magnetic resonance lines are, in general, much broader in the case of solids; the shape and observed splittings of such lines give valuable information regarding crystal structure. A related field of study in solids is called nuclear quadrupole resonance (NQR); absorption can be observed as a result of transitions between spatially quantized levels involving electrostatic interactions between the electric quadrupole moment of the nucleus and the resultant crystal field at its site.<sup>†</sup>

Radio frequency techniques are also employed to advantage in research involving molecular beams.<sup>†</sup>