

5.2: Nuclear Quadrupoles and Quadrupole-induced Relaxation

The above observations are the result of changes in the magnetic quantum numbers of the ^{14}N nuclei in substituted ammonium ions through interaction of the ^{14}N electric quadrupoles with surrounding asymmetrical electric fields. The mechanism for this is not so formidable as it might sound. In the first place, we noted earlier (pages 6 and 7) that nuclei with spins I of 0 or $1/2$ act as though their charges were distributed over a spherical surface. With those nuclei like ^{14}N having $I > 1/2$, however, the nuclear charge appears to be distributed over an ellipsoidal surface, and such nuclei act like electric quadrupoles. The symmetry axis of a nuclear quadrupole is collinear with the magnetic and angular momentum vectors of the nucleus. Now, consider a ^{14}N nuclear quadrupole such as the nitrogen of pyrrolidinium ion surrounded by a cloud of valence electrons which is not spherically symmetrical. The rapid tumbling motions of the ion in solution will cause a timevariable electric torque to be exerted on the quadrupole which will tend to shift the quadrupole orientation. Changes in the orientation of the quadrupole also result in changes in the direction of the magnetic vector of the nucleus. A relaxation mechanism is thereby provided for the ^{14}N nuclear magnet (see Fig. 5-2). Now, if the nitrogen nucleus of an ^{14}N -H compound is caused to flip back and forth among its several possible magnetic quantum states, the attached proton will "see" more or less of an average of three orientations of the nitrogen nucleus depending on the rate of Ripping.

In solutions of pyrrolidinium ion at room temperature, relaxation of the nitrogen nucleus takes place at a rate such as to render the hydrogens attached to the nitrogen somewhat confused as to the ^{14}N spin orientation. This results in broadened N-H proton resonance lines. At room temperature, the N-H line is intermediate between a singlet and triplet absorption, so that the mean lifetime of the nitrogen with a given magnetic quantum number is on the order of the reciprocal of $\nu_G/2$ times the triplet line separation, or about 0.009 sec. When the temperature is raised, the increased rate of tumbling of the molecules apparently results in less efficient nitrogen relaxation and the proton resonance goes to a broad triplet. When the temperature is lowered, the decreased tumbling rate allows for rather more efficient nitrogen relaxation and the triplet proton resonance lines coalesce to a broad singlet. Only a sharp triplet absorption is observed for nonexchanging ammonium ions because in these ions the electric field around the nucleus is spherically symmetrical and quadrupole-induced relaxation is not effective.

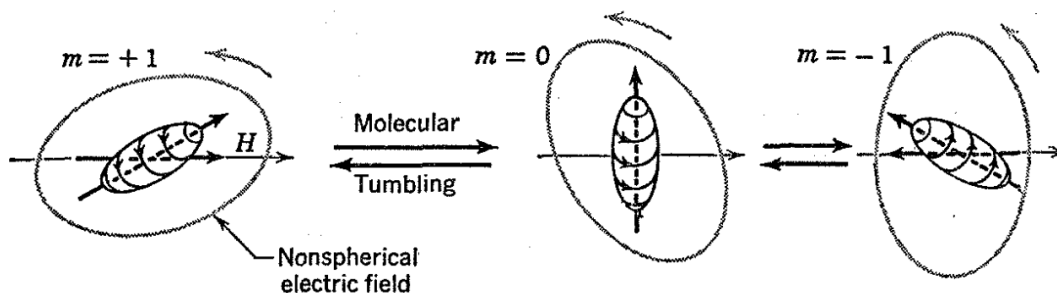


Fig. 5-2. Interaction of a nuclear quadrupole with an asymmetrical electrical field in a tumbling molecule. Horizontal line shows direction of applied magnetic field.

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