This Week's Citation Classic

CC/NUMBER 16
APRIL 20, 1981

Townes C H & Dailey B P. Determination of electronic structure of molecules from nuclear quadrupole effects. *J. Chem. Phys.* **17**:78296, 1949.
[Depts. Physics and Chemistry, Columbia University, New York, NY]

Nuclear quadrupole coupling constants in molecules depend on the nuclear quadrupole moment and the electric field gradient at the nucleus. An approximate method of calculating the electric field gradient is presented which permits the determination of molecular electronic structure from nuclear quadrupole coupling constants. [The *SCI*® indicates that this paper has been cited over 430 times since 1961.]

Benjamin P. Dailey
Department of Chemistry
Columbia University
New York, NY 10027

March 30, 1981

"This paper resulted from the collaboration of a physicist (Townes) and a chemist (Dailey), both interested in microwave spectroscopy and both working in the Columbia Radiation Laboratory where interesting equipment used for radar research was readily available. Both researchers, for somewhat different reasons, were interested in the problem of hyperfine structure due to nuclear quadrupole splitting associated with the energies of orientation of nuclei having less than spherical symmetry in the electric field gradient due to electrons and nuclei in atoms and molecules. I had been involved in an early study of this hyperfine splitting as observed in the microwave spectrum of ammonia. Townes's subsequent study of population transfer among the quadrupolar energy levels of ammonia was a prelude to his work on the maser and laser for which he received the Nobel prize in physics in 1964.

"Nuclear quadrupole coupling constants are a product of two factors: the nuclear quadrupole moment associated with the shape of the nuclear charge distribution, and the electric field gradient which is influenced by the electronic structure. As a physicist Townes was interested in nuclear quadrupole moments. It was hoped that they might cast some light on the theory of nuclear shell structure, a topic then of much current interest. Townes presented a seminar in which he outlined a possible method of obtaining the nuclear quadrupole moment from the nuclear quadrupole coupling constant by making an approximate calculation of the electric field gradient. At a certain level of approximation the field gradient could be thought of as largely determined by the shape of atomlike electron orbitals in the immediate neighborhood *of* the nucleus since the field gradient has a l/r^3 dependence and since spherical orbitals (s type) will make no contribution.

"After the seminar, I expressed great interest in the work to Townes. From his point of view, the approximate calculation of the field gradient was likely to give a rough value of one or two quadrupole moments, but to a chemist it was of greater interest to turn the problem around and use the nucleus as a probe of the molecular electronic structure where even approximate results would be *of* great value. Townes agreed to pursue this notion if I would work on the chemical end of the problem. After a somewhat lengthy but very pleasant period of collaboration the cited paper was written.

"The combination of a simple theory with in some cases simple and inexpensive experimental techniques has made this field of research quite popular. There have been at least two monographs written[1,2] (one in Russian) and several volumes of *Advances in Nuclear Quadrupole Resonance*.[3] Surprisingly, the paper, even after more than 30 years, has not yet been outmoded. The *ab initio* calculation of field gradients from accurate molecular wavefunctions is now possible for small molecules but has not proved as attractive as a moderately successful *simple* theory which permits comparison between series of similar molecules large enough to be of real chemical interest."

1. **Lncken E A C.** *Nuclear quadrupole coupling constants.* New York: Academic Press, 1969. 360 p.
2. **Semin G K, Babushkina T A & Yakobson G G.** *Nuclear quadrupole resonance in chemistry.* New York: Wiley, 1975. 517 p.
3. **Smith J A S,** ed. *Advances in nuclear quadrupole resonance.* London: Heyden, 19748. Vols. 13.