AD NUMBER

AD400768

NEW LIMITATION CHANGE

TO

Approved for public release, distribution unlimited

FROM

Distribution authorized to U.S. Gov't. agencies and their contractors; Foreign Government Information; DEC 1961. Other requests shall be referred to US Library of Congress, Attn: Aerospace Technology Division, Washington, DC.

AUTHORITY

ATD ltr, 2 Dec 1965

UNCLASSIFIED

AD __*400 760*__

DEFENSE DOCUMENTATION CENTER

FOR

SCIENTIFIC AND TECHNICAL INFORMATION

CAMERON STATION, ALEXANDRIA, VIRGINIA

UNCLASSIFIED

STEP

AUTHOR: Hsü, Kuang-chih (1776/1684/2535)

TITLE: Applications of nuclear quadrupole resonance in solid state chemistry

PERIODICAL: Hua Hsüeh T'ung Pao, no. 10, 1961, 1-8

TEXT: The nuclear quadrupole resonance spectrum was discovered by Dehmelt
and Krüger in 1949 and is used in solid state physics and structure chemistry. Nu-
clear quadrupole resonance was developed based on the following principles: (1) The
electromagnetic characteristics of atomic nuclei. Nuclei possess the characteristic
of self-spin. When the self-spin $I > 0$, a nuclear magnetic moment μ is developed.
When $1 > \frac{1}{2}$ an electric quadrupole moment is developed. The moment Q induced by
the nonspherical symmetrical distribution of positive charges in atomic nuclei is ex-
pressed by the following equation:

$$Q = \frac{1}{c} \int \rho(\theta, r)(3\cos^2\theta - 1)r^2 d\tau$$

$$= z(3z^2 - r^2)_{av} \qquad (1)$$

Card 1/7

Applications of nuclear quadrupole ...   F031/F003

where $\rho(\theta, r)$ = density of nuclear electronic charge, r = distance from mass center
to volumetric element $d\tau$, θ = angle between r and the self-spin axis, z = atomic
number. For elliptical distribution

$$Q = \frac{2}{5} z(r^2 - a^2) = \frac{8}{5} zR^2 \epsilon \qquad (2)$$

where $\epsilon = \frac{c - a}{c + a}$ = ellipse factor, $R = \frac{c + a}{2}$ (2) Energy levels and the corres-
ponding energy of Q in an inhomogeneous electric field. In an axially symmetric
field energy

$$E_M = \frac{cqQ}{4I(2I - 1)}\left[3M_1^2 - I(I + 1)\right] \qquad (3)$$

where q = electric field gradient at the nucleus, cqQ = the coupling constant of nuclear
quadrupole moment and $M_1 = I, I - 1, \ldots, -I - 1, -I$. If the induced frequency ν in an
inhomogeneous field satisfies the condition

$$h\nu = \Delta E = cqQ\left[\frac{3}{4I(2I - 1)}\right]\left[2|M_1| - 1\right] \qquad (4)$$

Card 2/7

transitions from one energy state to another will occur. If the energy state jumps
to a higher level, it results in the production of nuclear quadrupole resonances.
(3) Zeeman splitting theory. The introduction of an external magnetic field will
lead to further splitting of the energy levels. The process is called Zeeman splitting.
For simplicity, the energy of interaction of an axially symmetric quadrupole with an
axially symmetric electric field gradient is expressed by

$$E_M = \frac{cqQ}{4I(2I - 1)}\left[3M^2 - I(I + 1)\right] \pm M\frac{h}{2\pi} H\cos\theta$$

The magnetic field in which Zeeman splitting takes place is around 10^2 gauss with a
corresponding increase in frequency of 10^2 kc/sec. The frequency which satisfies
$\Delta M = \pm 1$ at $M > \frac{1}{2}$ and $\pm M \rightleftarrows \pm (M + 1)$ is given as

$$\omega_M^{\pm} = \frac{3cqQ}{\frac{h}{2\pi} 4I(I - 1)} (2|M| + 1) \pm r \cdot H\cos\theta$$

Card 3/7

(4) Factors affecting the spectral line width of the nuclear quadrupole resonance spectrum are: (1) Static factors. The function of adjacent dipoles between resonance nuclei and nonresonance nuclei will cause splitting in the resonance spectra and will also induce self-spin resulting in further fine splitting. Internal strain and misalignment of the samples and imperfection in the crystal lattice will also increase the width of spectral lines. (2) Kinetic factors. Molecular torsion and rotation are the principal causes. The movement is the result of an interelectronic function between adjacent molecules and can be estimated by means of an infrared detector and a Raman spectrum. Molecular rotation will change the electric field gradient as expressed by the following equation: $q' = q \left(\dfrac{3 \cos^2 \theta - 1}{2} \right)$ which in turn will affect the resonance frequency by the amount $\omega_{\infty} = \omega_8 \left(\dfrac{3 \cos^2 \theta - 1}{2} \right)$. The latter can be obtained from the resonance frequency-temperature curve. The installation for observation of nuclear quadrupole resonance spectra is similar to the equipment set up for nuclear magnetic

Card 4/7

resonance observations with the exception that a crystal field within a solid sample replaces the external magnetic field. The basic requirement is to regulate frequency changes and to record the resonance signals. The frequency ranges from a few kc to 1000 kc. Applications of the nuclear quadrupole resonance spectra are: (1) As a method of crystal analysis. Bray's papers point out that difference resonance spectra will show the existence of "unbalanced" atoms distributed in different parts of a crystal having varying electric field gradients. (2) As a method of ascertaining H bond formation in solids. Harry's experiment on Cl^{35} showed that the nuclear quadrupole resonance spectra can be used to determine the formation of H bonds in compounds. (3) As a method of studying phase changes in solids. The processes of phase changes in solids can be determined by the temperature change of the nuclear quadrupole spectra. (4) As a method of determining the ratios of nuclear quadrupole moments at different isotope effects. The relation between resonance frequencies is equivalent to the ratio of the nuclear quadrupole moments at different isotopic values. (5) As a method of studying the effects of radiation on matter. When solid matter is ex-

Card 5/7

posed to high energy radiations, changes will be induced in the electrons, free radicals, and unstable molecules resulting in the widening of resonance spectral lines. According to Monfils, the relationship satisfies the following equation:

$$I/I_0 = \exp^{-\nu_r \cdot c}$$

I and I_0 and are intensities of resonance spectra respectively before and after radiation, c - the concentration of impurities, and ν_r - the volumetric parameter relative to the amount of impurities. (6) As a method of studying the characteristics of chemical bonds. Since the electric field gradient can be calculated by the coupling constant and asymmetrical parameters of the nuclear quadrupole resonance under given conditions, the distribution of electronic charges and the characteristics of chemical bonds within the molecules can also be determined. The transition of valent electron to q in atoms is shown as follows:

$$q = -\rho_i \sum \int |\psi_i|^2 \left(\frac{3 \cos \theta_i - 1}{r_i} \right) d\tau,$$

Card 6/7

where ψ_i - the wave function of no. 1 p electron; r_i, Θ_i, and φ_i - polar coordinates of no. 1 p electron. The q value at atomic nucleus is determined by the degree of ioni a-tion, the degree of heterogeneity, and duplication of bond formation. (7) As a method of measuring internal stress of high polymers during processing operation. In 1960 Gutowsky successfully applied the nuclear quadrupole resonance method in measuring the internal stress of resins during vulcanization. Test results showed that this method excelled the optical and strain resistance methods. At present nuclear qua-drupole resonance spectrum is confined to the study of solids. According to Sterzer and Beers, the method is also applicable to the study of highly viscous liquids. The article was written with the assistance of Professors T'ang Yu-ch'i (0781/2589/438?) and Chien Jen-yüan (6929/0086/0337). There are 8 figures and 10 tables. English language references are: T. P. Das, E. I. Haha, "Nuclear Quadrupole Resonance Spectroscopy" 1958; F. Sterzer and Y. Beers, Phys. Rev., 100, 1174 (1955); H. S. Gutowsky, J. Polymer. Sci., 143, 143 (1960); P. L. Bray, Bull. Amer. Phys., 1 (2), 323 (1956).

Card 7/7