Rotational narrowing of nuclear magnetic resonance spectra

Autor(en): **Andrew, E.R.**

Objekttyp: **Article**

Zeitschrift: **Archives des sciences [1948-1980]**

Band (Jahr): **12 (1959)**

Heft 8: **Colloque Ampère : Maxwell-Ampère conference**

PDF erstellt am: **30.06.2024**

Persistenter Link: https://doi.org/10.5169/seals-739103

Nutzungsbedingungen

Die ETH-Bibliothek ist Anbieterin der digitalisierten Zeitschriften. Sie besitzt keine Urheberrechte an den Inhalten der Zeitschriften. Die Rechte liegen in der Regel bei den Herausgebern.
Die auf der Plattform e-periodica veröffentlichten Dokumente stehen für nicht-kommerzielle Zwecke in Lehre und Forschung sowie für die private Nutzung frei zur Verfügung. Einzelne Dateien oder Ausdrucke aus diesem Angebot können zusammen mit diesen Nutzungsbedingungen und den korrekten Herkunftsbezeichnungen weitergegeben werden.
Das Veröffentlichen von Bildern in Print- und Online-Publikationen ist nur mit vorheriger Genehmigung der Rechteinhaber erlaubt. Die systematische Speicherung von Teilen des elektronischen Angebots auf anderen Servern bedarf ebenfalls des schriftlichen Einverständnisses der Rechteinhaber.

Haftungsausschluss

Alle Angaben erfolgen ohne Gewähr für Vollständigkeit oder Richtigkeit. Es wird keine Haftung übernommen für Schäden durch die Verwendung von Informationen aus diesem Online-Angebot oder durch das Fehlen von Informationen. Dies gilt auch für Inhalte Dritter, die über dieses Angebot zugänglich sind.

Ein Dienst der *ETH-Bibliothek*
ETH Zürich, Rämistrasse 101, 8092 Zürich, Schweiz, www.library.ethz.ch

http://www.e-periodica.ch

Rotational Narrowing of Nuclear Magnetic Resonance Spectra

by E. R. Andrew

Physics Department, University College of North Wales,
Bangor, Caernarvonshire

Résumé.

On étudie l'amincissement des spectres de résonance magnétique nucléaire de solides obtenu par rotation rapide de l'échantillon. On examine la forme des raies d'origine dipolaire ainsi amincies et on en déduit la réduction du second moment de ces raies. On discute en outre la rotation d'un cristal contenant des molécules tournantes et on montre que dans certains cas favorables, l'axe de rotation moléculaire peut être déterminé. On discute encore les effets de la rotation sur les spectres élargis:

1° par l'inhomogénéité du champ;
2° par l'échange entre spins nucléaires;
3° par l'anisotropie du déplacement chimique ou du « Knight shift »;
4° par les interactions électriques quadrupolaires.

Les effets étant différents dans chaque cas, l'observation du spectre d'un échantillon en mouvement rapide de rotation doit aider à déterminer l'origine de l'élargissement du spectre.

Abstract.

The narrowing of *nmr* spectra of solids by rapid macroscopic rotation of the specimen is discussed. For dipolar-broadened spectra the shape of the narrowed spectrum is considered and the reduction of its second moment is derived. The rotation of a crystal containing rotating molecules is also discussed, and it is shown that the axis of molecular rotation may in suitable cases be determined. A discussion is also given of the effects of rotation on spectra broadened by *(a)* field inhomogeneity, *(b)* nuclear spin exchange, *(c)* anisotropy of chemical shift or Knight shift, *(d)* electric quadrupolar interactions. Since the effects are different in each case, observation of the spectrum of the rapidly-rotated specimen should assist in determining the sources of spectral broadening.

Last year we reported an experiment which showed that the rapid rotation of a crystal causes its dipolar-broadened nuclear magnetic resonance spectrum to become narrower [1]. The situation is closely similar to that encountered when molecules rotate within a solid which, as is well-known, also causes spectral narrowing [2]. There are two significant differences however. First, when the whole crystal rotates, all nuclear pairs rotate with the same constant angular velocity and so generate observable resonance side-spectra spaced at multiples of the frequency of rotation on either side of the narrowed spectrum [3]. On the other hand when molecules rotate within a static crystal, the nuclear pairs move with a random motion embracing a wide range of rotational frequencies; the side-spectra are in this case dispersed over a wide band of frequencies and are too weak for observation. Secondly all nuclear separations remain the same when the entire crystal is rotated, whereas when molecules rotate within a crystal only intra-molecular or intragroup distances remain the same. For the rotating crystal all nuclear separations are effectively intra-molecular and no distinction between intra- and inter-molecular interactions is necessary; the calculation of the spectral narrowing is therefore simpler and the experimental spectra provide a more direct quantitative demonstration of the narrowing.

The second moment S of a dipolar-broadened spectrum is given by Van Vleck's celebrated formula [4]:

$$S = \frac{1}{3}\left(\frac{\gamma}{2\pi}\right)^2 \hbar^2 \sum_k \varepsilon_k^2 \gamma_k^2 I_k (I_k + 1) (3 \cos^2 \theta_k - 1)^2 r_k^{-6} \; . \qquad (1)$$

In this expression γ is the gyromagnetic ratio of the resonant nuclei, and the sum is taken over all the nuclear neighbours of a typical resonant nucleus; if there are a number of crystallographically different nuclear sites a weighted mean over all sites is taken. γ_k is the gyromagnetic ratio of the k^{th} neighbour, I_k is its spin number, r_k is its distance, θ_k is the polar angle which the vector r_k makes with the applied field, and ε_k is $\frac{3}{2}$ if the neighbour is another resonant nucleus, and is unity if not.

When the crystal rotates rapidly about an axis normal to the applied field, as in the experiment, each θ_k varies cyclically. Each term $(3 \cos^2 \theta_k - 1)$ must be replaced by its time-average since it occurs in the interaction Hamiltonian from which (1) was derived, and must be replaced by its expectation value. This time-average is $-\frac{1}{2}(3 \cos^2 \psi_k - 1)$, where ψ_k is the angle between the vector r_k and the rotation axis. The second moment of the central spectrum for the rotating crystal is therefore

$$S_{\text{rot}} = \frac{1}{12}\left(\frac{\gamma}{2\pi}\right)^2 \hbar^2 \sum_k \varepsilon_k^2 \gamma_k^2 I_k (I_k + 1) (3 \cos^2 \psi_k - 1)^2 r_k^{-6} \; . \qquad (2)$$

Comparison of (1) and (2) gives the quite general result that when a crystal is rotated about an axis perpendicular to the field, the second moment is precisely $\frac{1}{4}$ of that for the static crystal when oriented with the field along the rotation axis. Indeed since every term in the interaction Hamiltonian is halved, the resonance spectrum should have the same shape but just half the width. [1]

Thus in an experiment in which a sodium chloride crystal was rotated about its [100] axis with the field in the (100) plane, the central spectrum should have the same shape but half the width, and a quarter of the second moment, as for the static crystal with the field along the [100] axis. Within experimental error we found this to be the case.

For polycrystalline material the angular factors in (1) and (2) must be replaced by their isotropic averages, which in both cases are $\frac{4}{5}$. There is now no directional preference in the specimen and the spectrum is isotropic. Rotation halves the dipolar width of the central spectrum, reducing the second moment to a quarter of its static value.

Suppose now we rotate a crystal within which there are rotating molecules. The average of $(3 \cos^2 \theta_k - 1)$ must now be found over both the microscopic and the macroscopic motions. If the rotation axis is perpendicular to the field this average turns out to be $-\frac{1}{4}(3 \cos^2 \psi_k - 1)(3 \cos^2 \alpha_{12} - 1)$, where α_{12} is the angle between the two rotation axes. If the two rotation axes are coincident, α_{12} is zero, and rotation of the crystal has caused no further reduction in second moment; this is to be expected on physical grounds. On the other hand if the two rotation axes are different $(3 \cos^2 \alpha_{12} - 1)$ will be less than its maximum value of 2, and rotation of the crystal will cause a further narrowing of the spectrum. In this way an axis of molecular rotation within a crystal could in suitable cases be determined.

For polycrystalline material, whose dipolar second moment is already reduced by molecular motion within the crystallites, calculation shows that

---

[1] If the axis of rotation is not normal to the applied field butmakes an angle α with the field, then the width is reduced by a factor $\frac{1}{2} \mid 3 \cos^2 \alpha - 1 \mid$. If α has the value $\cos^{-1} (1/\sqrt{3}) = 54° 44'$, the dipolar broadening ofthe central line should there fore be removed entirely.

the further reduction of the second moment caused by rotation of the entire specimen is in all cases a further factor $\frac{1}{4}$.

Now let us consider the effect of rotating a specimen whose spectral width does not originate primarily in the magnetic dipolar interactions between the nuclei so far discussed.

1. *Broadening due to field inhomogeneity.* The situation here is the same as that encountered in recording high resolution n.m.r. spectra of liquids. If the specimen is rapidly rotated about the Z axis, the effective field experienced by the nuclei is, to a first order, the average field in each xy plane. Rotation of the specimen therefore largely removes inhomogeneity broadening in the xy plane leaving only the effects of inhomogeneity along the axis of rotation. The rotation produces sidebands at integral multiples of the rotation frequency on either side of the narrowed line [5]. This contrasts with the narrowing of a dipolar-broadened line for which sidebands occur only at even multiples of the rotation frequency, the odd multiples being absent.

2. *Broadening due to nuclear spin exchange.* Indirect electron-coupled nuclear interactions of the form $a\mathrm{I}_i \cdot \mathrm{I}_j$ are responsible for the multiplet splitting of high resolution n.m.r. spectra of liquids. For heavy nuclei these interactions can be important in solids also [6, 7], in some cases dominating the spectrum. These interactions are rotationally invariant, and for this reason rapid molecular motion in a liquid does not obliterate them. For the same reason rotation of a solid specimen will also have no effect on this source of spectral broadening.

3. *Broadening due to anisotropy of chemical shift or of Knight shift.* For simplicity we confine the discussion here to cases where the nucleus has an environment with axial symmetry. For a polycrystalline specimen the spread of resonance frequencies caused by the anisotropic shift gives an asymmetrical spectrum ranging from $\nu_0 (1 + \delta_1)$ to $\nu_0 (1 + \delta_2)$ where there is a singularity; ν_0 is the resonance frequency for the free nucleus, δ_1 is the shift along the symmetry axis and δ_2 is the shift perpendicular to the axis. This asymmetrical profile is the main feature of the spectrum for tetragonal tin [7]. If the specimen is rotated at a frequency greater than $\nu_0 (\delta_1 - \delta_2)$, the average shift field experienced by each nucleus must be calculated. We find that the spectrum now ranges from $\nu_0 (1 + \delta_2)$, where there is no

longer a singularity, to $\nu_0 \left[1 + \frac{1}{2}(\delta_1 + \delta_2)\right]$, where a singularity appears. The new spectrum has just half the width of the static spectrum, has the same geometrical shape but with the asymmetry reversed, and has the same mean frequency $\nu_0 \left[1 + \frac{1}{3}(\delta_1 + 2\delta_2)\right]$.

4. *Broadening due to electric quadrupolar interactions.* A situation of interest here is the second-order broadening of the centre-line of a quadrupole-split spectrum of a nucleus of half-integral spin. If there is axial symmetry the frequency of the central line is [8]

$$\nu_0 + \mathrm{B}\,(1 - 9\cos^2\theta)\sin^2\theta\,, \tag{3}$$

where θ is the angle between the symmetry axis and the applied field, and where the constant B is

$$\frac{9}{256} \cdot \frac{2\mathrm{I} + 3}{\mathrm{I}^2\,(2\mathrm{I} - 1)} \cdot \frac{e^4\,\mathrm{Q}^2\,q^2}{h^2\,\nu_0}\,,$$

where $e^2\,\mathrm{Q}q/h$ is the quadrupole coupling constant. In a polycrystalline specimen the angles θ are distributed isotropically, causing the centre line to be spread over a range of frequencies from $\left(\nu_0 - \frac{16}{9}\mathrm{B}\right)$ to $(\nu_0 + \mathrm{B})$, with singularities at each end of the range, a small discontinuity at ν_0, and a mean frequency of $\left(\nu_0 - \frac{8}{15}\mathrm{B}\right)$, [8]. This line profile has been observed by Silver and Bray in boron oxide glass [9].

If now the specimen is rapidly rotated the mean perturbation must be found for each crystallite. Calculation shows that the spectrum now extends from $\left(\nu_0 - \frac{23}{27}\mathrm{B}\right)$ to $(\nu_0 + \mathrm{B})$ with singularities at $\left(\nu_0 - \frac{23}{27}\mathrm{B}\right)$ and at $\left(\nu_0 - \frac{5}{8}\right)$, and with a mean frequency still at $\left(\nu_0 - \frac{8}{15}\mathrm{B}\right)$. The spectrum is in fact appreciably narrower and its shape is changed.

The quadrupolar-broadened spectrum from nominally cubic crystals containing defects is therefore a smooth superimposition of spectra of the type just discussed corresponding to a distribution of values of B over the nuclear sites. Rotation should therefore narrow each component spectrum in the same manner, thus narrowing the whole spectrum.

Summarising we see that rotation of a specimen affects its nuclear magnetic resonance spectrum in different ways depending on the interaction responsible for the broadening. Rotation may therefore assist in determining the interactions responsible.

1. Andrew, E. R., A. Bradbury and R. G. Eades, *Nature*, *182*, 1659 (1958) and *Arch. Sci.*, *11*, 223 (1958).
2. Gutowsky, H. S. and G. E. Pake, *J. Chem. Phys.*, *18*, 162 (1950).
3. Andrew, E. R. and R. A. Newing, *Proc. Phys. Soc.*, *72*, 959 (1958).
4. Van Vleck, J. H., *Phys. Rev.*, *74*, 1168 (1948).
5. Williams, G. A. and H. S. Gutowsky, *Phys. Rev.*, *104*, 278 (1956).
6. Ruderman, M. A. and C. Kittel, *Phys. Rev.*, *96*, 99 (1954).
7. Bloembergen, N. and T. J. Rowland, *Acta Metallurgica*, *1*, 731 (1953).
8. —— *Phys. Soc. Bristol Conference*, 1 (1954).
9. Silver, A. H. and P. J. Bray, *J. Chem. Phys.*, *29*, 984 (1958).