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Linewidths in High-Resolution NMR Spectra.
Homogeneous Broadening due to Intermolecular Dipolar Relaxation.

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Abstract
The effects connected with the intermolecular relaxation in the coupled nuclear systems are studied theoretically. It was shown that, because of general properties of nuclear-spin systems, the number of parameters necessary to describe the relaxation process is reduced reduced substantially. Moreover, the structure of nuclear system and the relaxation process parameters are to a large extent separated. This fact enables one to draw quite detailed conclusions about the energy level widths even without any specification of the type of intermolecular relaxation process.

Keywords: NMR, NMR spectroscopy, HR-NMR, Linewidth, Relaxation, Dipolar relaxation, Coupled system

Erratum: A factor of 2 is missing in the second term of Eq.(8). Consequently, the values of the R_{ij} functionals must be multiplied by 2.

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imum uncertainty in the measurements is estimated to be less than 2%. The temperature and ortho–para composition dependences of our dilute gas measurements are in good agreement with dilute gas viscosities and approximate theoretical calculations of the modified Eucken factor. The thermal conductivity of compressed liquid hydrogen increases with both density and temperature and is independent of ortho–para composition within our precision. We observe that the temperature dependence of the liquid at fixed densities is considerably larger than for other simple fluids with the exception of helium. In the critical region the thermal conductivity of hydrogen increases rapidly as the temperature and density approach their critical values.

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[1] J. W. Stewart, J. Chem. Phys. **40**, 3297 (1964).
[2] H. M. Roder, L. A. Weber, and R. D. Goodwin, Natl. Bur. Std. (U.S.), Monograph 94 (1965).
[3] A. Michels and J. V. Sengers, Physica **28**, 1238 (1962).
[4] J. B. Ubbink, Physica **14**, 165 (1948).
[5] H. L. Johnston and E. R. Grilly, J. Chem. Phys. **14**, 233 (1946).
[6] I. F. Golubev and M. V. Kalsina, Gaz. Prom. **9**, 41 (1964).
[7] E. A. Mason and L. Monchick, J. Chem. Phys. **36**, 1622 (1962).
[8] R. J. Munn, F. J. Smith, E. A. Mason, and L. Monchick, J. Chem. Phys. **42**, 537 (1965).
[9] D. E. Diller and E. A. Mason, J. Chem. Phys. **44**, 2604 (1966).
[10] H. J. M. Hanley (private communication).
[11] J. V. Sengers, *Recent Advances In Engineering Science*, edited by A. C. Eringen (Gordon and Breach, New York, 1968), Vol. 3, p. 159.
[12] B. J. Bailey and K. Kellner, Physica **39**, 444 (1968).
[13] H. Ziebland and J. T. A. Burton, Brit. J. Appl. Phys. **9**, 52 (1958).
[14] J. F. Kerrisk and W. E. Keller, Phys. Rev. **177**, 341 (1969).
[15] R. W. Powers, R. W. Mattox, and H. L. Johnston, JACS **76**, 5972 (1954).
[16] N. V. Tsederberg, *Thermal Conductivity of Gases and Liquids* (MIT Press, Cambridge, Mass., 1965).
[17] D. J. Elzinga and G. Thodos, J. Spacecraft Rockets **5**, 868 (1968).
[18] A. Michels, W. DeGraaff, T. Wassenaar, J. M. H. Levelt, and P. Louwerse, Physica **25**, 25 (1959).

Linewidths in High-Resolution NMR Spectra. Homogeneous Broadening Due to Intermolecular Relaxation

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The effects connected with the intermolecular relaxation in the coupled nuclear systems are studied theoretically. It was shown that, because of the general properties of nuclear-spin systems, the number of parameters necessary to describe the relaxation process is reduced substantially. Moreover, the structure of nuclear system and relaxation process parameters are to a far extent separated. This fact enables one to draw quite detailed conclusions on the energy-level widths even without any specification of the type of intermolecular relaxation process.

This paper is a direct continuation of a preceding one[1] (I) in which the intramolecular dipolar broadening in coupled nuclear systems was studied. It is based on the first two sections of I (basic theory and its restrictions); there are however many other connecting points between the two papers which are referred to.

I. DISCUSSION OF THE PERTURBING MAGNETIC FIELD

Let us denote $\bar{h}_i(t)$ as that component of the magnetic field on the nucleus i which results from intermolecular interactions. Then $\bar{h}_i(t)$ is a vector function of time with a stationary random character. Its mean value is very small (except in ferromagnetic samples) and can be included in the chemical shift of the nucleus i. For simple noncoupled systems this procedure

is equivalent to the correction for magnetic susceptibility of the sample. The corrected fluctuating magnetic field $\bar{h}_i(t)$ now becomes

$$\bar{h}_i(t) = \mathbf{h}_i(t) - A_\sigma\{\mathbf{h}_i(t)\}, \tag{1}$$

where A_σ is the statistical averaging operator (see I).

For the description of relaxation processes, the correlation functions connected with $\bar{h}_i(t)$ must be known. Let us imagine a molecule in the sample as being fixed with respect to a laboratory coordinate system. Furthermore, let us consider two directions defined by means of two unit vectors $\bar{l}$ and $\bar{l}'$. Then the correlation function between the $\bar{l}$ component of the random field on nucleus i and the $\bar{l}'$ component of the random field on nucleus j is defined as

$$\mu_{ij}(\bar{l}, \bar{l}'; \tau) = A_\sigma\{[\bar{l}\cdot\bar{h}_i(t)][\bar{l}'\cdot\bar{h}_j(t+\tau)]\}. \tag{2}$$

TABLE I. The values of R functionals in the AB system.[a]

r	Eigenvector	$R_A{}^0 = R_B{}^0$	$R_A = R_B$	$R_{AB}{}^0 = R_{BA}{}^0$	$R_{AB} = R_{BA}$	$2\Gamma^R(r)/\gamma^2$
1	$\lvert \alpha\alpha \rangle$	0	1	0	0	$J(\Phi)$
2	$\cos\varphi \lvert \alpha\beta \rangle + \sin\varphi \lvert \beta\alpha \rangle$	p^2	1	$-p^2$	p	$J(\Phi) + \{J(0) - j(0)\}p^2 + j(\Phi)p$
3	$\cos\varphi \lvert \beta\alpha \rangle - \sin\varphi \lvert \alpha\beta \rangle$	p^2	1	$-p^2$	$-p$	$J(\Phi) + \{J(0) - j(0)\}p^2 - j(\Phi)p$
4	$\lvert \beta\beta \rangle$	0	1	0	0	$J(\Phi)$

[a] $J(\omega) = J_A(\omega) + J_B(\omega)$; $j(\omega) = J_{AB}(\omega)$; $p = \sin 2\varphi$; $\tan 2\varphi = \mathcal{J}/\delta$; and $\mathcal{J}, \delta$ are the coupling constant and the chemical shift of the AB system, respectively.

Because the molecule disturbs the isotropy of the surrounding medium in a very complicated way owing to its shape, no general rules can be given for the dependence of $\mu_{ij}(\bar{l}, \bar{l}'; \tau)$ on the parameters $\bar{l}, \bar{l}'$. In the high-resolution conditions, of course, the molecule is not fixed: it rotates randomly. As far as the medium is isotropic, all orientations of the molecule are equally probable. With spatially fixed vectors $\bar{l}, \bar{l}'$ the $\mu_{ij}(\bar{l}, \bar{l}'; \tau)$ can not depend on the absolute orientation of these two vectors. Consequently, a relation must hold of the type

$$\mu_{ij}(\bar{l}, \bar{l}'; \tau) = \mu_{ij}'(\cos\theta; \tau), \qquad \cos\theta = \bar{l} \cdot \bar{l}'. \quad (3)$$

The dependence of μ_{ij}' on $\cos\theta$ is still quite general. Nevertheless, Relation (3) permits one to define two correlation functions which only will be important in the following discussion:

$$G_{ij}(\tau) = \mu_{ij}'(1; \tau) = A_\sigma\{h_i{}^a(t) h_j{}^a(t+\tau)\}, \quad (4a)$$

$$g_{ij}(\tau) = \mu_{ij}'(0; \tau) = A_\sigma\{h_i{}^a(t) h_j{}^b(t+\tau)\}, \quad (4b)$$

where $a, b = x, y, z$ with $a \neq b$, and $h_i{}^a(t)$ is the a component of the vector $\bar{h}_i(t)$.

As emphasized above, Relation (3) holds only in an isotropic medium. If we leave aside liquid crystals with their evident anisotropy, there still remains the possibility that the originally isotropic medium will be linearly polarized after the application of the principal magnetic field. The possible sources of the random magnetic fields $\bar{h}_i(t)$ have not yet been considered. The typical examples are: magnetic moments of nuclei and electrons, induced magnetic fields in the electron structure of randomly moving molecules, magnetic fields connected with the motions of charged or dipolar molecules, etc. Since the perturbation energy due to the magnetic field is quite negligible in comparison with the energies of thermal motion, the magnetic field can not significantly polarize the molecular motions and positions. It influences, of course, the polarization of the present magnetic moments of any kind and induces highly polarized magnetic moments in molecular electron structures. But a simple direct calculation shows that the magnetic field of an homogeneously distributed polarized magnetic dipole has an isotropic distribution at any point of space. Equations (4) are consequently valid for any system which is isotropic in the absence of magnetic field and the inner energy of which changes negligibly by the application of the field. On the basis

of the correlation functions (4) two spectral density functions can be defined for every pair of nuclei i and j:

$$J_{ij}(\omega) = L_\omega G_{ij}(\tau); \qquad j_{ij}(\omega) = L_\omega g_{ij}(\tau), \quad (5)$$

where L_ω is the Fourier-transform operator (see I).

II. BROADENING OF ENERGY LEVELS

With the random fields (1) the perturbation Hamiltonian due to intermolecular interactions has the form

$$H' = \sum_k H_k'(t),$$

$$H_k'(t) = \gamma_k \bar{I}_k \cdot \bar{h}_k(t) = \tfrac{1}{2}\gamma_k\{K_k h_k{}^z + I_k{}^+ h_k{}^- + I_k{}^- h_k{}^+\}, \quad (6)$$

where the subscript k denotes the nucleus and γ_k and $\bar{I}_k$ are its gyromagnetic ratio and spin-vector operator, respectively. The convention $\hbar = 1$ is used and $K_k = 2I_k{}^z$, $h_k{}^\pm = h_k{}^x \pm h_k{}^y$.

It is now possible to proceed in the same way as in I. Because the relations

$$(I_i{}^\pm)_{rs}(I_j{}^\pm)_{sr} = 0 \quad (7)$$

are valid for any two nuclei i and j and for any two eigenstates r and s, the probability $\mathcal{W}_{rs}$ of the transition $r \to s$ under the influence of the perturbation $H'(t)$ becomes

$$\mathcal{W}_{rs} = \sum_{i,j} \mathcal{W}_{rs}(i, j),$$

where

$$\mathcal{W}_{rs}(i, j) = \tfrac{1}{4}\gamma_i\gamma_j\{(K_i)_{rs}(K_j)_{sr}J_{ij}(0)$$
$$+ e_{ij}[(I_i{}^+)_{rs}(I_j{}^-)_{sr} + (I_i{}^-)_{rs}(I_j{}^+)_{sr}]J_{ij}(\Phi_i)\}. \quad (8)$$

Here e_{ij} equals 1 if the nuclei i and j are of the same kind and is zero otherwise, and Φ_i is the resonance frequency of the nucleus i.

A somewhat surprising but very convenient fact is the absence in Eq. (8) of the spectral density function $j_{ij}(\omega)$; this is a consequence of (7).

The intermolecular interactions involving the nuclei i and j contribute to the width of the rth energy level by a term $\Gamma_{ij}{}^R(r)$. The summation process discussed in I leads to the following formula:

$$\Gamma_{ij}{}^R(r) = \tfrac{1}{4}\gamma_i\gamma_j\{R_{ij}{}^0(r)J_{ij}(0) + R_{ij}(r)J_{ij}(\Phi_i)\}, \quad (9)$$

where the functionals $R_{ij}{}^0$ and R_{ij} are defined as

$$R_{ij}{}^0(r) = (K_iK_j)_{rr} - (K_i)_{rr}(K_j)_{rr}$$

and

$$R_{ij}(r) = e_{ij}(I_i^+I_j^- + I_i^-I_j^+)_{rr}. \tag{10}$$

The total contribution $\Gamma^R(r)$ of the intermolecular interactions to the width of the rth energy level results in a sum of the terms $\Gamma_{ij}{}^R(r)$ for all pairs of nuclei i and j. The one-particle terms $(i=j)$ and two-particle terms $(i \neq j)$ may be distinguished. In the one-particle case the R functionals (10) may be written in a simpler form:

$$R_i{}^0(r) = R_{ii}{}^0(r) = (K_i{}^2)_{rr} - (K_i)_{rr}{}^2,$$

$$R_i(r) = R_{ii}(r) = 2S_i(S_i+1) - \tfrac{1}{2}(K_i{}^2)_{rr}, \tag{11}$$

where S_i is the total spin value for the nucleus i. For spin-$\tfrac{1}{2}$ nuclei

$$R_i{}^0(r) = 1 - (K_i)_{rr}{}^2, \qquad R_i(r) = 1. \tag{12}$$

As will be shown in the following paragraph, the one-particle terms are expected to be dominant. For systems composed of spin-$\tfrac{1}{2}$ nuclei and, moreover, non-symmetrical and relatively weakly coupled the $(K_i)_{rr}$ values are nearly equal to ± 1 and, consequently, the $R_i{}^0(r)$ are very small. In such a case the $\Gamma^R(r)$ values are approximately equal for all the energy levels which leads to a roughly equal broadening of all transitions by the intermolecular interactions.

III. DISCUSSION OF THE SPECTRAL DENSITY FUNCTIONS

As was shown in Sec. II, only one spectral density function $J_{ij}(\omega)$ is needed for each pair of nuclei i and j. $J_{ij}(\omega)$ is connected with the correlation function $G_{ij}(\tau)$ by the defining equation (5). Because the source of the perturbing magnetic field was not explicitly specified, the $G_{ij}(\tau)$ coinvolve all the necessary information on all the intermolecular relaxation mechanisms. It is the task (which is anything but easy) of the statistical theory of fluids to determine the way in which the individual interaction mechanisms contribute to the $G_{ij}(\tau)$. Nevertheless, some properties of these functions are expected to be general.

Firstly, both $G_{ij}(\tau)$ and $J_{ij}(\omega)$ must be rapidly decreasing functions of the distance between the nuclei i and j. A rough picture of what happens might be obtained by putting $J_{ij}(\omega) = 0$ for all $i \neq j$ (zero-correlation approximation). Such an approximation will probably be too crude if there is any substantial correlation between mutual molecular positions (polarization by

molecular dipole moments, solvation, complex formation, etc). Even in these cases, of course, the dominant character of the one-particle terms can hardly be invalidated.

In I an approximation was used in which the following relation holds[2] for all the correlation functions:

$$\tilde{G}_{ij}(\tau) = G_{ij}(\tau)/G_{ij}(0) \doteq \exp(-|\tau|/\tau_c'), \tag{13}$$

where $\tilde{G}_{ij}(\tau)$ are reduced correlation functions and τ_c' is the characteristic correlation time, connected here with the intermolecular relaxations. As results from the discussion in paragraph I, the $G_{ij}(\tau)$ are influenced by the translational as well as rotational behavior of molecules. It is therefore impossible to connect the τ_c' directly with the diffusion coefficients or with the viscosity of the sample. If (13) is valid, the spectral densities are given by

$$J_{ij}(\omega) = \tfrac{2}{3}A_\sigma\{\bar{h}_i \cdot \bar{h}_j\}\{\tau_c'/(1+\omega^2\tau_c'^2)\}. \tag{14}$$

Moreover, if $\omega\tau_c' \ll 1$ (fast reorientation limit), then $J_{ij}(\omega) = J_{ij}(0)$ and the dominant one-particle spectral density functions become

$$J_i(\omega) = J_i(0) = \tfrac{2}{3}\tau_c'A_\sigma\{\bar{h}_i{}^2\}. \tag{15}$$

IV. APPLICATIONS

In I, several simple systems were discussed in order to show more directly the basic features of the broadening due to the intramolecular dipolar relaxation. With respect to the simplicity of the equations (9–12), a similar discussion would have only restricted value in the case of the intermolecular relaxation effects. As a simple example the values of R functionals and the resulting energy level widths in the AB system are given in Table I. As long as $J_{AB}(\Phi) \ll J_A(\Phi) + J_B(\Phi)$, the same linewidths result for all transitions of the AB quartet independently of the strength of the coupling between the nuclei A and B; a fact which yet emphasizes the remarks at the end of Sec. II.

The symmetrical systems must be treated with particular attention. Thus, for example, in an A_2 system the equienergetical states 2 and 3 belonging to different symmetry types are mutually coupled by the perturbation terms (6). As discussed in I, the present theory can not be used in such a case.

[1] S. Sýkora, J. Chem. Phys. **52**, 4818 (1970).
[2] A. Abragam, *The Principles of Nuclear Magnetism* (Clarendon, Oxford, England, 1961).