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MÖSSBAUER EFFECT IN LIQUIDS: INFLUENCE OF DIFFUSION BROADENING*

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Measurements of the Mössbauer effect can yield information relating to phonon spectra in solids.[1] Under appropriate circumstances the resonance can also be observed in liquids,[2] and such measurements yield information relating to diffusion effects during the nuclear state lifetime. We report here measurements on cobalt-57 chloride in glycerol and on Co^{57} embedded in the organic molecules porphyrin and hemoglobin, from which effective sizes for the diffusing objects are deduced. A further result relates to the Mössbauer recoil process and shows that in the presence of large diffusion effects the massive molecules do not recoil independently in the fluid, but rather the recoil momentum is transmitted to the entire fluid mass.

Diffusion broadening in neutron scattering from liquids has been discussed by Vineyard.[3] His analysis has been explicitly applied to Mössbauer scattering by Singwi and Sjölander.[4] They find the probability for recoil-free emission of a photon in the presence of diffusion to be proportional to

$$\exp[-R/4k_BT]\int \exp[i(\vec{k}\cdot\vec{r}-\omega t)-(\Gamma/2\hbar)|t|]\times F_s^{\,c}(\vec{r},t)\,d\vec{r}\,dt, \qquad (1)$$

where $R=E_\gamma^2/2mc^2$ is the classical recoil energy of a diffusing body of mass m following the emission of a photon of energy $E_\gamma=\hbar kc$. The state lifetime is $\tau=\hbar/\Gamma$ and $E-E_\gamma=\hbar\omega$. $F_s^{\,c}(\vec{r},t)$ in Eq. (1) denotes the classical self-diffusion function, which in the case of a simple diffusive type of motion is given by the solution to the classical self-diffusion equation with diffusion constant D:

$$F_s^{\,c}(\vec{r},t)=(4\pi D|t|)^{-3/2}\exp(-r^2/4D|t|). \qquad (2)$$

The intensity of the recoil-free emission of a photon of energy E is then

$$I(E)=\frac{(I_0/2\pi)(\Gamma+2\hbar k^2D)}{(E-E_\gamma)^2+\frac{1}{4}(\Gamma+2\hbar k^2D)^2}, \qquad (3)$$

a Lorentzian spectrum centered at E_γ with width $\Delta\epsilon=\Gamma+2\hbar k^2D$.

We have observed experimentally the broadening $\Delta\epsilon$ of the recoil-free emission line as the diffusion constant increases. The 100-nsec 14-keV gamma level in Fe^{57} was used, and because of the small effects expected with broad lines, the experiments were performed using liquid sources containing the parent nuclide (270-day Co^{57}) rather than liquid absorbers. The procedure circumvents difficulties encountered in absorber experiments arising from gamma-ray attenuation in the nonresonant atoms comprising the host molecules. In order to obtain diffusion constants of the requisite magnitude (10^{-10} to 10^{-8} cm^2/sec), glycerol was used as a solvent. By variation of the temperature, the viscosity η and hence T/η could be varied over several orders of magnitude. The efficacy of glycerol for this purpose and the applicability of macroscopic viscosity measurements to atomic processes has been demonstrated by Bloembergen.[5] Neutron studies of diffusion in glycerol have been made by Larsson and Singwi.[6]

Sources of cobalt-57 chloride in glycerol were prepared by adding nominally carrier-free cobalt-57 chloride in HCl to glycerol. A $(99.5\pm0.5)\%$ glycerol sample was prepared by pumping on the solution for about one week. The glycerol concentration was determined by direct measurement at 27°C of the viscosity of a similarly prepared but nonradioactive solution. Values for the viscosity of water-glycerol solutions in the temperature range of interest (-50°C to 0°C) were obtained by normalizing the extrapolated measurements of Tammann and Hesse[7] to the more recent high-temperature measurements of Segur and Oberstar.[8] The broadening of the narrower lines was studied by using an unsplit isotopically enriched absorber [$K_2Fe(CN)_6 \cdot 3H_2O$]. The absorber used in the studies of the broader lines was metallic Fe (1.7 mg/cm^2 Fe^{57}). Hyperfine splitting in the Fe absorber increased the apparent resonance strength by a factor of about six.

In Fig. 1 we present measurements of the source linewidth minus the natural linewidth divided by the natural linewidth for cobalt-57 chloride dissolved in glycerol as a function of T/η. At the lowest values of T/η, $(\Delta\epsilon - \Gamma)/\Gamma$ becomes constant, a type of behavior characteristic of resonances in glasses.[9] At higher temperatures, $(\Delta\epsilon - \Gamma)/\Gamma$ increases linearly with T/η. In principle, the values of $\Delta\epsilon$ may be corrected for the linewidths observed at very low temperatures; this procedure decreases slightly the deviation of the points in Fig. 1 from the line. At the lowest temperatures the emission line was split by quadrupole interactions into two lines separated by (2.6 ± 0.1) mm/sec. At higher temperatures, where this splitting could no longer be resolved, it was subtracted from the observed linewidths. The experimental line shapes were approximately Lorentzian, and the diffusion widths were obtained by direct subtraction of the widths of the resonant absorbers.

The diffusion constant of a sphere of radius a in a viscous medium is $D = k_B T/6\pi\eta a$. From our measurements on cobalt-57 chloride in glycerol, we obtain $(\Delta\epsilon - \Gamma)/\Gamma = (160 \pm 35)T/\eta$ (°K/poise). The radius of the diffusing object is calculated to be (0.65 ± 0.14) Å. Since the Co^{57} decays to iron, this value may be compared with the crystal radii of Fe^{++} (0.75 Å) and Fe^{+++} (0.60 Å).[10] It should be noted, however, that these radii are considerably smaller than those expected for this system.

The dependence of the linewidth upon the radius of the host molecule was studied by substituting Co^{57} for Fe in hemin (molecular weight 620) and hemoglobin (molecular weight 64 450).[11] The measurements were consistent with a linewidth linear in T/η. For hemin, $(\Delta\epsilon - \Gamma)/\Gamma = (75 \pm 25) \times T/\eta$, while for hemoglobin $(\Delta\epsilon - \Gamma)/\Gamma = (15 \pm 5) \times T/\eta$ (°K/poise). The coefficients of T/η obtained by scaling the results in cobalt-57 chloride as the cube root of the mass ratios are 72 ± 16 and 15 ± 3, respectively, agreement which is certainly fortuitous. From the known diffusion constant of hemoglobin in water at 20°C, the radius of the hemoglobin molecule is found to be 27 Å.[12] The value calculated from our measurements is (7.4 ± 2.5) Å. The radius calculated from our measurements is again lower than that determined in other studies. This apparent discrepancy may arise, in part, from the dissociation of the hemoglobin into smaller units in glycerol.

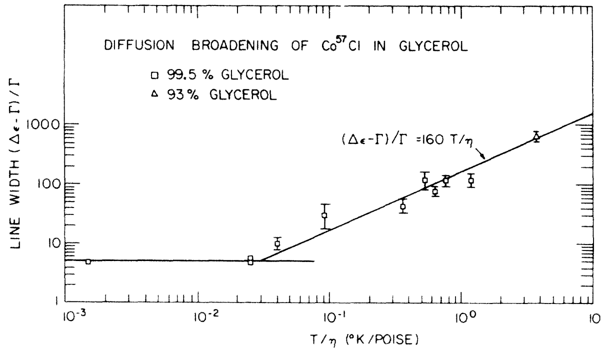

FIG. 1. Diffusion broadening of the Mössbauer resonance for a source of Fe^{57} in glycerol. The observed linewidth (in units of the ideal linewidth) varies linearly with the temperature of the glycerol solute divided by its viscosity as expected from a classical diffusion model.

Quadrupole splitting of (2.0 ± 0.2) mm/sec was found in hemoglobin at 1.5°K, 4°K, and 77°K, and of (1.8 ± 0.2) mm/sec in hemin at 170°K.

No attempts were made to measure accurately the recoil-free emission probabilities. For the materials studied these probabilities were estimated to be approximately 20% and relatively independent of the diffusion linewidths. Such a value is, on a Debye model, consistent with the Debye temperature 150°K found for glycerol from neutron scattering by Larsson and Singwi[6] and is below the value predicted from the theory of Singwi and Sjölander.[4]

The line positions in all cases were within 0.2 mm/sec of zero velocity where quadrupole splitting could be resolved and within about 10% of the linewidths of zero velocity for the broader lines. The ratio of the diffusion linewidth to the classical recoil energy R' calculated for the entire molecular weight M is $\Delta\epsilon/R' = 4DM/\hbar$, independent of Γ and E_γ. For a 14-keV gamma ray emitted by a source in hemoglobin, the velocity shift corresponding to R' is $cR'/E_\gamma = 3.8$ cm/sec (or 2.5 cm/sec for an effective hydrodynamic mass of $3M/2$). For the largest line broadenings we have observed in hemoglobin, $\Delta\epsilon = 0.23R'$, while the observed shift δ is less than $0.02R'$. This absence of shift is in agreement with Vineyard's theory of diffusion effects for neutrons.[3]

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HIGH-RESOLUTION NUCLEAR MAGNETIC RESONANCE SPECTRA OF ORIENTATED MOLECULES

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We have studied nmr spectra of liquid crystals, especially of the nematic type and of solutions in nematic liquids. We should like to discuss here briefly some of our results. (More extensive papers will appear elsewhere.)

Nematic liquids are homogeneously ordered by the magnetic field applied in nmr experiments. The rodlike molecules are orientated more or less completely parallel to the field. For a full description of the molecular average orientation, a symmetric matrix must be used with the elements $S_{ij} = \frac{1}{2}\langle 3\cos\theta_i \cos\theta_j - \delta_{ij}\rangle_{\text{av}}$ $(i, j = \xi, \eta, \zeta;$ δ_{ij} Kronecker symbol). ξ, η, ζ are the axes of a Cartesian coordinate system fixed in the molecule, and θ_i their angles with the field.

There is no regular arrangements of centers and the molecules retain a high mobility (low viscosity). The intermolecular direct dipole-dipole interaction is therefore averaged out as in isotropic liquids. The reorientation of the molecules, as could be shown from dielectric measurements[1] with PAA (p-azoxyanisole, $R\text{-O-}C_6H_4\text{-}N_2O\text{-}C_6H_4\text{-O-}R$ where $R = CH_3$), is at least in some cases also sufficiently rapid to reduce the intramolecular interactions to sharp average values. But here in contrast to isotropic liquids the anisotropic part of the interactions is not lost because of the molecular orientation. The pmr (proton magnetic resonance) spectrum of PAA, for instance, should therefore consist of a large number of sharp lines extending over a range of some 20 kc/sec.

The spectrum of the nematic phase of PAA has been extensively studied by several authors[2] and has been described as a broad diffuse triplet. We could find a very detailed fine structure in agreement with the above considerations (Fig. 1). With further improved resolution even more details are to be expected. If the methyl groups are replaced by larger groups ($R = C_nH_{2n+1}$, $n = 2$ to 7), the spectra become quasicontinuous due to the strongly increased number of lines.

In the spectra of the nematic phase of p-butoxybenzoic acid ($C_4H_9OC_6H_4COOH$), a strong and very sharp line superimposed on a broad background signal has been observed. This line is assigned