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MOLECULAR MOTIONS IN A VISCOUS ORGANIC LIQUID:

FERROCENE IN COLD BUTYL PHTHALATE

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NOTICE

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Introduction:

We have made extensive studies of the ferrous atom surrounded by six H_2O (the ferrous hexaquo-ion) in hydrochloric and phosphoric acid glasses and liquids. We had anticipated relaxation effects for the electric field gradient interaction caused either by a) flickering changes in the detailed distances of the six nearest oxygen ions causing jumps in the EFG direction, or b) diffusive rotation of the whole ion. Such rotational effects have not been seen, and part of the motivation for this work was to choose a system where the second of the above mechanisms would be made more likely. Briefly put, can rotational diffusion for simple molecules be seen along with the well-known translational effect?

Another development from the phosphoric acid work [1] has been the recognition of the rapid decrease in peak area (alternately a rapid increase in $\langle x^2 \rangle$) seen as glasses are heated above T_g , the glass transition temperature. Previous work [2] has focussed mainly upon the line width $\Gamma(T)$, and had shown that translational diffusion seemed to vary directly with the viscosity, but no quantitative use has been made of the amplitude information. It seemed desirable to add an organic glass-liquid system to the previous aqueous work, and to measure $2W(T) = \langle x^2(T) \rangle / \lambda^2$ below and above T_g . Would dissimilar liquids show any similarity of response?

Some Experimental Details:

To maximize the rotational effects, a 'round' non-bonding molecule like ferrocene [3] seemed an obvious choice. Its large molecular

quadrupole splitting of some 2.4 mm/sec is quite suitable for quadrupole relaxation measurements. So ferrocene dissolved in some organic liquid would be suitable, if the liquid could be cooled without crystallization. This requirement forced us to eliminate many simple organic liquids (e.g. benzene) which promptly crystallize on cooling. After some work (and occasional weak crystallizations) using butyl benzene, our system became butyl phthalate (BuPh) which readily dissolves ferrocene, and doesn't crystallize.

Differential thermal analysis measurements were made which gave

$T_g = 175 (\pm 1) \text{ K}$. Most of the measurements were made using 91% enriched ferrocene (we wish to thank Prof. T. Marks of Northwestern for this preparation); the concentration was about 1 ferrocene molecule per 200 BuPh.

The MB measurements were routine. The source used was Co^{57} in Cu. The spectra at higher temperature were carried to several million counts/channel, and the fractional dips at low temperatures are $> 30\%$. As the temperature increases, the dips decrease in amplitude due to line broadening and relaxation effects, from the ordinary decrease in $f(T)$ in a weakly bound glass, and eventually from the more rapid decrease of f in a liquid. Thus careful examination of blurry spectra is needed, and much care was taken to overcome instrumental effects. For one, the small absorption due to iron impurity in the Be window of the proportional counter was measured (by setting the absorber temp at 260 K), and included in all the other spectra. For another, the slight baseline curvature resulting from a moving source was removed as part of the data handling procedure. Temperatures were controlled by regulators to better than $\pm .2 \text{ K}$.

Careful measurements were taken to allow the use of a transmission integral program; this requires accurate knowledge of the signal and background for the detected 14.4 keV γ -rays. The broadened, but constant line width below T_g of 0.24 was accounted for by assuming a constant source line width of 0.14 mm/sec, cf. $\Gamma_0 = 0.10$ mm/sec.

Spectral Shapes and Curve Fitting Procedures:

The main theoretical treatment of this problem evolves from work of Tjon and Blume [4], and has been made particularly appropriate for this problem by Dattagupta [5]. The first authors have treated the problem of a stochastically jumping EFG direction, and have given the resultant line shape in a simple closed form expression as a function of a rotation width (or inverse frequency). Dattagupta has extended the problem to include time-synchronized translational diffusion along with the rotational diffusion. In the first paper of Ref. 5, the results are given for the case where jumps of length r occur stochastically at a rate $\lambda = 1/\tau_j$ and at the end of each jump, the direction of the EFG is arbitrary. This strong rotation model could perhaps have been appropriate to the case of flickering readjustments of the positions of the nearest neighbor oxygens in the phosphoric acid case. The second paper of [5] describes a more general result where after each jump, the EFG has changed, but by an amount corresponding to a rotational diffusion constant d . This line shape is given (eq. 17) as:

$$S(p) = \text{Real} \left\{ \frac{p + \lambda(1 - g(k)) + 6dg(k)}{[p + \lambda(1 - g(k))][p + \lambda(1 - g(k) + 6dg(k)) + (QS/2)^2]} \right\}, \quad (1)$$

where $p = -i(\omega - \omega_0) + \frac{1}{2}\tau$.

Recent work on the phosphoric acid system [6], in contrast with some earlier experiments [7, 8], indicate that the jump distance r is at least an order of magnitude less than a typical interatomic spacing. And molecular dynamics strongly suggests [9] that the 'jumps' are so small that a continuous random diffusion constant D is all that has much meaning. In this paper we shall adopt the continuous random diffusion model, for which $r \rightarrow 0$ in such a way that $g(k) = \int e^{i k \cdot r} g(r) dr \rightarrow 1 - k^2 D \tau_j$. Here $k = 1/\lambda$ is the photon propagation vector, and $D (= r^2/6\tau$ when there is a jump distance r) is the translational diffusion constant. Now Eq. (1) is simplified:

$$S(p) = \text{Real} \left\{ \frac{p + k^2 D + 6d}{(p + k^2 D + 6d)(p + k^2 D) + (QS/2)^2} \right\} \quad (2)$$

The relation between d and D is not at all clear. For molecules in a gas, rotational frequencies are very high ($\sim 10^{12}$ per second). But the quadrupole splitting would appear blurred in a ^{57}Fe Mössbauer measurement with rotation angles of a radian or so in 10^{-7} seconds. It is easy to believe that rotational effects will appear rather strongly unless as in a true solid, the molecules are firmly bonded against rotation. On the other hand, in the macroscopic, classical limit case, Stoke's law gives $d = D/a^2$ where a is the particle radius. If this law applies to a single molecule, then $k^2 D + 6d$ becomes $k^2 D [1 + (6/4\pi^2) * (\lambda/a)^2] = k^2 D [1 + .04]$ for $\lambda/a = .5$. Clearly, if $6d$ is small compared to $k^2 D$, the observation of rotational effects will be difficult.

This suggests that unless a $\langle \lambda \rangle$ (impossible for ^{57}Fe experiments, since $\lambda = 0.86 \text{ \AA}$), the effects due to rotation will always be hard to observe compared to translational diffusion effects. It is convenient to define $\alpha = 6d/k^2 D$ as a measure of the importance of rotation. And we shall try to find it experimentally.

In Fig. 1, spectra at four temperatures are displayed. All the spectra below 175 K look much like the curve for $T = 179.7 \text{ K}$. Above 175 K, the lines broaden slowly, but decrease in intensity rapidly. Even at our highest temperature (limited by the rapidly dropping $f = e^{-2W(212)} \cong e^{-6.7} \cong 0.001$), the shape is roughly a doublet whose lines have broadened to about 1 mm/sec. This already suggests that rotation here is weak. As mentioned above, a small amount of background absorption is visible near zero velocity.

If $d \rightarrow 0$,

$$S = \text{Real} \left[\frac{\frac{1}{2}}{p + k^2 D + i QS/2} + \frac{\frac{1}{2}}{p + k^2 D - i QS/2} \right], \quad (3)$$

which is readily seen to be two Lorentzian lines of width $(1/2 \tau) * (1 + 2k^2 D)$ centered at $\pm QS/2$ in the velocity (energy) scale. This is of course the well-known translational diffusion result. However, if $d \rightarrow \infty$,

$S = \text{Real} \left[\frac{1}{p + k^2 D} \right]$ which is merely a translationally broadened Lorentzian centered at zero velocity (the quadrupole splitting has relaxed completely to a singlet). In general, Eq. (2) expresses a pair of translationally broadened lines QS apart, but where d (or α) is relaxing them toward the

center. In Fig. 7a of the preceding phosphoric acid paper, line shapes are shown for $\alpha = .1$ for various value of the temperature. Despite differences in parameters such as $QS(T)$ and $D(T)$, the meaning of this figure is also suitable for ferrocene. The temperature dependence of f due to $2W$ has been omitted, so that the experiments seem easier than in fact they are. The results (mainly each line broadens as T increases) was anticipated by Eq. (3) above.

Fig. 7b, for $\alpha = 1$, shows that for T too low or too large the line shape is not sensitive to α . But for intermediate values, in this case for T near 200 K, the central collapse is well underway for $\alpha = 1$, and had α been this large, it would have been seen in these experiments.

It is desirable to clarify the difference between these line shape calculations and those reported by Gunther and Wilcox [10]. They are interested in large particles, and the Mössbauer atom is not restricted to the center, so for them variations in the rotation angle cause changes in the velocity. If the particle is a stiff, non-diffusive solid, then the observation of the effects of rotation on the line shape will not be strongly hindered, as in our case, by the increasing thermal vibrations and diffusion. Our results, and also Dattagupta's Eq. [1], are confined to molecules with the MB nucleus at the center of mass. It is desirable to generalize this restriction.

The shape of Eq. (2) was included in a curve fitting procedure where the adjustable parameters were the baseline, the absorber thickness $t = n\sigma e^{-2w}$, isomer shift $s = s_c - c \cdot \frac{\langle v^2 \rangle}{2c^2}$, and the translational diffusion broadening $GD = 2k^2 D \tau_J$. It was not possible to

leave α as a parameter of the fit since it interacted too strongly with the other parameters. Instead, the fittings were made for a series of values of α (0, .01, .1, .125, .25, .5, 1, 2, 4, 8, ∞) although not for all the temperatures measured.

Considerable care was taken with the programming to reduce systematic errors. For one, a finite channel width correction was made; this was useful for the rather sharp lines below T_g . More importantly, a transmission integral was included in the calculation of line shapes so that the large variations in t between low and high temperature did not introduce systematic distortions.

Corrections for the Gol'danski'i-Karyagin effect were not taken. Measurements on solid ferrocene had shown a substantial G-K effect [$\epsilon = 2w_{11} - 2w_{12} = -0.8$ at 200 K]; however, in solution, the asymmetry parameter ϵ never decreased below -0.2, and was in fair agreement with a curve calculated on the assumption that the liquid was isotropic, and only the molecular vibrations reported from IR measurement [11] ($\theta_{11} = 245$ K; $\theta_{12} = 689$ K) were active. An ϵ this small would not seriously affect our fitting procedure, especially since the symmetric shape program has no parameter capable of simulating the 'tilt' produced by ϵ . This neglect should only result in negligible increases of χ^2 .

Results for $\langle x^2 \rangle$ and $\langle v^2 \rangle$:

One result of the fittings was $t(T)$. This quantity was treated to produce $2W(T) = \ln(n\sigma_0) - \ln(t)$, where $n\sigma_0 = 48.9$ comes from the number of iron atoms used. A temperature independent chemical shift was subtracted from the experimental isomer shifts to produce the second order Doppler shift $s_v = C \cdot \langle v^2 \rangle / 2c^2$. The fitted values for t and s were quite independent of α . $2W$ and s_v have been plotted in Fig. 2. Examining the lower half of Fig. 2, the slope of the isomer shifts is noticeably less than that for a soft lattice. This reminds us that this glass should be rather clearly divided into high frequency Einstein-like molecular modes and a continuum of much softer Debye modes for the heavy molecule in this poorly bonded system.

We adopt a model of a molecule of mass 187 $[\text{Fe}(\text{C}_5\text{H}_5)_2]$ with a Debye spectrum whose maximum temperature $k\theta_D = \hbar\omega_m$ allows for the low frequency modes; and also we use the two perpendicular molecular modes at 245 K and the single parallel one at 689 K for an iron atom of mass 57 [7]. The sum of these motions should produce $\langle v^2 \rangle$ and $\langle x^2 \rangle$, at least below T_g . There is a problem in normalization reflecting our ignorance of the detailed behaviour of the higher frequency modes in this complicated situation. But this problem can be solved by using a normalization such that at very high T , v^2 should be classical $= \frac{3kT}{m}$. This model must now account for both $2W$ and s_v below T_g .

Let

$$N(\omega) = \beta \frac{9N\omega_m^2 d\omega}{3} + (1 - \beta) 3N \left\{ \frac{2}{3} \delta(\omega \sim 245) + \frac{1}{2} \delta(\omega \sim 689) \right\} \quad (4)$$

be the normal mode distribution remembering that the Debye modes refer to $M = 187$ and the Einstein ones to $m = 57$. As usual

$$v^2(\omega) = \frac{\hbar\omega}{2mN} \frac{1 + e^{-y}}{1 - e^{-y}}; \quad x^2(\omega) = \frac{\hbar\omega}{2m\omega^2 N} \frac{1 + e^{-y}}{1 - e^{-y}}, \quad (5)$$

where $y = \hbar\omega/kT = \theta/T$. The number β describes the division between molecular and Debye modes.

To extend the model above T_g , we adopt the idea that some of the continuum modes go "soft," and reappear at lower energy θ_E . The simplest version of this is to replace:

$$\beta \frac{9N\omega_m^2 d\omega}{3} \quad \text{with} \quad \beta \epsilon \frac{9N\omega_m^2 d\omega}{3} + \beta (1 - \epsilon) 3N \delta(\omega \sim \theta_E), \quad (6)$$

where ϵ represents the unshifted fraction of Debye modes. After some algebra, one gets

$$s_v = c \cdot \frac{1}{2} \cdot \frac{3kT}{2mc} \cdot A \left[\beta \epsilon \frac{m}{M} v_D^2(\theta_D) + \beta (1 - \epsilon) \frac{m}{M} x_E^2(\theta_E) + (1 - \beta) v_M^2 \right] \quad (7)$$

and

$$2W = \frac{E^2}{2mc^2} \cdot \frac{1}{k300} \cdot A \left[\beta \epsilon \frac{m}{M} 3 x_D^2 (\theta_D) + \beta (1 - \epsilon) \frac{m}{M} x_E^2 (\theta_E) + (1 - \beta) x_M^2 \right]. \quad (8)$$

Here $A = M/(M(1 - a) + ma)$. Also

$$v_D^2(\theta) = \left(\frac{T}{\theta}\right)^3 \int_0^\theta y^3 \frac{1 + e^{-y}}{1 - e^{-y}} dy; \quad x_D^2(\theta) = \frac{300}{\theta} \left(\frac{T}{\theta}\right)^2 \int_0^\theta y \frac{1 + e^{-y}}{1 - e^{-y}} dy \quad (9)$$

and

$$v_E^2(\theta) = y \frac{1 + e^{-y}}{1 - e^{-y}}; \quad x_E^2(\theta) = \frac{300}{T} \left(y \frac{1 + e^{-y}}{1 - e^{-y}} \right) \quad (10)$$

and

$$v_M^2 = \frac{2}{3} v_E^2 \left(\frac{245}{T} \right) + \frac{1}{3} v_E^2 \left(\frac{689}{T} \right); \quad x_M^2 = \frac{2}{3} x_E^2 \left(\frac{245}{T} \right) + \frac{1}{3} x_E^2 \left(\frac{689}{T} \right). \quad (11)$$

Since θ_D and θ_E are small, we use the high temperature limits. Then $v_O^2 = \frac{2}{3}$, $v_E^2 = 2$, $x_D^2 = 600T/\theta_D^2$, and $x_E^2 = 600T/\theta_E^2$. Now (7) and (8) become

$$s_v = 0.212 \text{ mm/s} \left[\gamma \frac{T}{300} + (1 - \gamma) \frac{T}{300} \frac{v_M^2}{2} \right] \quad (12)$$

$$2W = 0.1172 \left[\gamma \frac{1200 T}{\theta_D^2} + (1 - \gamma) \frac{2}{3} x_M^2 + \gamma d(T - T_g) \frac{400 T}{\theta_E^2} \left(1 - 3 \frac{\theta_E^2}{\theta_D^2} \right) \right], \quad (13)$$

where we have put

$$\epsilon = \begin{cases} 1 & T < T_g \\ 1 - d(T - T_g) & T > T_g \end{cases} \text{ and } \gamma = \frac{m/M}{r + m/M}, \text{ and } r = \frac{1 - a}{a}.$$

By subtracting the isomer shift values from the chemical shift,

s_v is found. By assuming that this shift does not depend on temperature, a plausible guess for this molecule, the experimental points for s_v can

be shifted vertically as desired. s_c must be such that the experimental points lie between the purely molecular and purely solid-like lines. Further, Eq. (12) shows that s_c can be any weighted average of the limiting cases. Our choice ($s_c = 0.33$ mm/sec vs Fe in Cu) determines $\gamma = 0.20$. The two Einstein molecular modes are weighted by 80%; all the solid-like Debye modes are only 20%. We note further that s_v in Eq. (12) does not depend on ϵ , while x^2 in Eq. 13 does.

The line labeled 'glass' in Fig. 2a corresponds to the above choice of γ and $\theta_D = 47.5$ in Eq. 13; it fits the data below T_g quite well. Above T_g , we invoke ϵ to shift some of the Debye modes to a lower temperature θ_E . The data for x^2 required $d/\theta_E^2 = 4.3 \times 10^{-5}$. If $\theta_E = 5K$, the fraction of shifted modes near room temperature $d(T - T_g)$ becomes 10% which is probably too small. For $\theta_E = 10K$, nearly 50% of the solid-like Debye modes have been shifted to lower energy. The model is too precise - there is not a single low frequency θ_E , the number of shifted modes does not have to be proportional to the temperature above T_g , γ has not been determined with any accuracy, etc. However, the picture of a heavy stiff molecule (v^2 is nearly all explained by the molecular vibrations) shaking in jellium with $\theta_D \approx 50K$ does fit both v^2 and x^2 up to T_g . The abrupt experimental increase in x^2 (and flat behaviour of v^2) could be explained formally by a decreasing θ_D . Alternately, and hopefully more physically, this model suggests that the transverse vibrational modes are progressively being weakened as the glass becomes less viscous.

Quadrupole Splitting:

A word about curve fitting will be useful. Looking at Fig. 7 of the other paper, one would at first expect that, when α was not appropriate to the data, then the calculated curve will not fit and χ^2 , or some similar fitting statistic like MISFIT, would be too large. This will only be true if the fitting routine cannot find any other trick, no matter how dishonest, to fulfill its prime overriding aim - to decrease χ^2 !! Frequently, the program can use another parameter of the program and, by giving it improper values, still manage to keep χ^2 fairly small. This is not too common in simple programs in which the parameters may be "orthogonal" to each other. But for complicated programs, it is not enough to find reasonable χ^2 at every temperature: one must still require that the behaviour of each parameter with temperature be reasonable.

As mentioned in the preceeding paper, the quadrupole splitting is sensitive to the value of α . If α is too large, the quadrupole splitting appears reduced, and if QS is a free parameter in a fitting routine, an improper high value of QS will be chosen to compensate for this. In Fig. 3 we show the fitted values for QS vs temperature for numerous values of α . Note that QS in solid ferrocene is quite constant.

Below 180 K, regardless of α , all the fits show the quadrupole splitting is decreasing slowly with temperature. This is not understood, but is not unreasonable. It would be quite desirable to know this temperature dependance from an independent measurement. Above 205 K, the curves for large α turn rather abruptly away from this trend. As indicated above, this 'unreasonable' behaviour probably indicates that $\alpha > 1$ is incorrect. A likely statement from this evidence is: α is less than 0.5. Without independent knowledge of e^2qQ , one cannot be more precise.

For a given sample, there will be a temperature at which $6d$ is several times $1/\tau_n$, and one will see rotational relaxation if neither $2W$ nor D is too large. These constraints, plus Stokes law, imply that an ordinary rotational relaxation is unlikely to be seen. But in a system such as Fe^{2+} impurities in MgO , the direction of the excess $3d$ electron wave on each impurity may fluctuate, but neither $2W$ nor D has to be large. Another distant possibility is the rotation of a coin-like molecule in a layered medium; observation perpendicular to the layers might keep D and $2W$ small, even though there is fast rotation about one axis.

Diffusion Constant versus T:

The value for D depends slightly on α . In Fig. 4, we show results for $\alpha = 0$ (no rotation) for $c \cdot \hbar^2 k^2 D/E_y = \Delta \Gamma$ and for D plotted against $1/T$.

Conclusions:

Rotational relaxation is not visible even in this case of a spherical non-bonded molecule in a liquid.

Extra vibrational amplitude $\langle x^2 \rangle$ is created quickly as the material is warmed above T_g . This is associated with 'soft' modes. It is not that the transverse modes of the liquid simply disappear with decreasing viscosity, but that they are shifted to lower energies.

Footnotes and References:

- * Work performed under the auspices of the Energy Research and Development Administration and the National Science Foundation.
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Figure Captions:

Fig. 1: Experimental absorption spectra for 180, 204, 209, and 212 K.

The absence of appreciable rotational relaxation of the EFG is evident. $\Delta\Gamma = \hbar k^2 D \cdot c / E \frac{\text{mm}}{\gamma \text{ sec}}$, assuming $d = 0$.

Fig. 2: $2W$ and s_v vs temperature. Experimental data from ferrocene in BuPh. The calculations are described in the text, but both curves involve the same dynamical assumptions.

Fig. 3: The quadrupole splitting parameter vs temperature, as determined by the fitting program for numerous values of α , for ferrocene in BuPh. The open boxes refer to solid ferrocene crystal.

Fig. 4: The translational diffusion constant vs temperature for ferrocene in BuPh.

Figure 1
(209-76-518, PHG 13537)

Figure 2
(209-76-440, PHG 13492)

Figure 3
(209-76-438, PHG 13490)

Figure 4

(209-76-437, PHG 13489)