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A comparison of the rough sphere rotational diffusion model with experimental results for liquid methyl iodide

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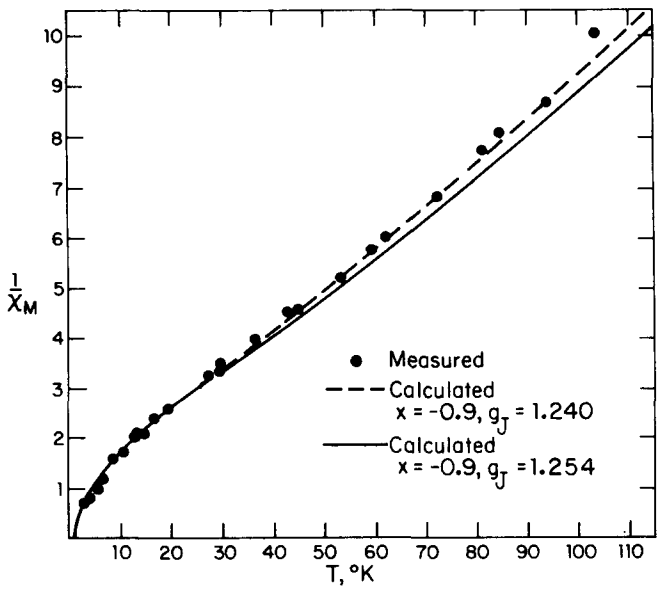

FIG. 1. Data fitted by calculated reciprocal magnetic susceptibilities for $Cs_2NaY(Cf)Cl_6$.

Fock) calculation given by Lewis *et al.*,[12] $\langle r^4\rangle \approx 5$ a. u. and $\langle r^6\rangle \approx 35$ a. u. for Cf^{3+}, so $A_4 = (90 \pm 30)$ cm^{-1}/a. u. and $A_6 = (1.7 \pm 0.7)cm^{-1}$/a. u. The corresponding values for Dy^{3+} are $A_4 = (120 \pm 20)cm^{-1}$/a. u. and $A_6 = (4.6 \pm 2)$ cm^{-1}/a. u.[9] Given the relatively large uncertainties in both these cases, the values of A_4 and A_6 for Cf^{3+} and for Dy^{3+} are approximately equal. Thus, the increased crystal field effects in the actinide compounds are primarily due to the larger values for the radial parameters $\langle r^n\rangle$.

A simple comparison of the radial parameters Cf^{3+} and Dy^{3+} would have suggested a much larger sixth-order contribution in the actinides than in the lanthanides due to the increased $\langle r^6\rangle$ from the more extended $5f$ electrons. The effect of the larger $5f\langle r^6\rangle$ is largely counteracted by the strong reduction in γ when that parameter is obtained from intermediate coupling wavefunctions. A previous magnetic susceptibility study[2] of the trivalent actinide compounds Cs_2NaMCl_6 ($M = U^{3+}$, Pu^{3+}, etc.) was interpreted as consistent with a range in the ratio $A_6^0\langle r^6\rangle/A_6^0\langle r^4\rangle$ between 0.31 and 0.034. The present value for Cf^{3+}, 0.18, falls within this range.

The above calculation of χ assumes first-order theory and does not include configuration interaction or J-mixing contributions. Substantial contributions from configuration interactions were found in a spectral study[13] of $CfCl_3$, and configuration interaction could alter the relative spacing of the crystal field levels from the LLW first-order model or even the ordering of the levels, as found in EPR studies[14] on Pu^{3+}. Configuration interactions might be the cause of the divergence between the data and theory above 50 °K. Because the next higher state in $CfCl_3$ was found[12] at 6500 cm^{-1}, J mixing is presumed to be unimportant.

Finally, the present analysis gives a Γ_6 crystal field ground state for Cf^{3+}, with a $\Gamma_8^{(1)}$ level as the first excited state at ~50 cm^{-1}. The total crystal field splitting is calculated to be approximately 860 cm^{-1}.

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A comparison of the rough sphere rotational diffusion model with experimental results for liquid methyl iodide

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The rotational motion of molecules in the liquid state has been described using several models. Chandler has recently developed a theory which describes rotational motion in terms of a system of rough hard spheres interacting through binary collisions.[1] This model, which provides a microscopic derivation of Gordon's J-diffusion model,[2] has been tested against molecular dynamics results[1,3] and spin–spin and spin–lattice NMR relaxation time results.[4] To our knowledge, no detailed comparisons have been made between Chandler's

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theory and Raman and infrared experimental results. It is the purpose of this note to present such a comparison. We use methyl iodide for testing the theory, as both infrared and Raman data for this molecular liquid are accurately known.

Chandler's rough hard sphere model pertains strictly to a system of spherical particles undergoing instantaneous collisions. As a result of a collision, one particle transfers angular momentum to the particle with which it collides. For smooth spheres, the collisions are still instantaneous but no transfer of angular momentum takes place. A realistic model for nonspherical molecules, such as CH_3I, would probably lie between these extremes of "smooth" and "rough", as was pointed out by Chandler. In his paper, Chandler gives theoretical expressions for the rotational correlational functions $C_1(t)$ and $C_2(t)$ and the zero-frequency relaxation times τ_1 and τ_2 which correspond to the experimental infrared and Raman zero-frequency rotational relaxation times, respectively. The final forms of the equations are

$$\tau_1 = \int_0^\infty C_1(t)\,dt = \tau_\omega x e^x E_1(x)/[1 - x e^x E_1(x)] \tag{1}$$

and

$$\tau_2 = \int_0^\infty C_2(t)\,dt = \tau_\omega[1 + 3ye^y E_1(y)]/4\{1 - \tfrac{1}{4}[1 + 3ye^y E_1(y)]\} \tag{2}$$

where $x = I/2\tau_\omega^2 kT$, $y = I/8\tau_\omega^2 kT$, I is the moment of inertia, T is the absolute temperature, and k is Boltzmann's constant. τ_ω is essentially the angular momentum correlation time and is related to the Enskog relaxation time τ_E through the relation $\tau_\omega^{-1} = a\tau_E^{-1}$, where a is the roughness of the hard sphere. For perfectly smooth hard spheres $a = 0$, and for perfectly rough hard spheres $a = [(4I/md^2) + 1]^{-1}$, where m is the molecular mass and d is the molecular diameter. τ_E is given by

$$\tau_E^{-1} = \tfrac{8}{3}(\pi kT/m)^{1/2}\rho d^2 g\,, \tag{3}$$

where ρ is the particle density. g, the contact value of the hard sphere radial distribution function, equals $(2-\eta)/2(1-\eta)^3$ with η, the packing fraction, equal to $(\pi/6)\rho d^3$. The function $E_1(z)$ is given by

$$E_1(z) = \int_z^\infty \frac{e^{-u}}{u}\,du\,. \tag{4}$$

Chandler compared the predictions of his theory to molecular dynamics results for liquid nitrogen. Nitrogen is a linear molecule with a length-to-width ratio of ~1.3. The theoretical values of τ_2 agreed with the molecular dynamics results for a roughness of 0.43 (the perfectly rough sphere roughness for N_2 is ~0.83). The theoretical τ_1 values were generally lower than the molecular dynamics results. O'Dell and Berne have performed molecular dynamics experiments for a rough sphere fluid and compared the results to the predictions of Chandler's theory.[3] The theoretical relaxation times were consistently larger than the molecular dynamics times. DeZwann and Jonas have studied CCl_3F and SF_6 using spin–echo and spin–lattice NMR techniques.[4] From the spin–lattice relaxation time measurements,

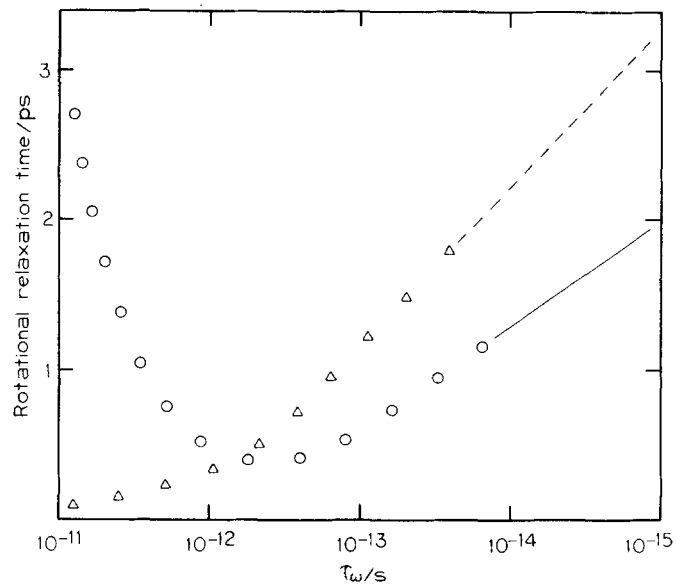

FIG. 1. Rotational relaxation times versus angular momentum relaxation time for methyl iodide at 283.7 K: ΔΔΔ, τ_1 (infrared); ---, τ_1 (extrapolated); ooo, τ_2(Raman); ——, τ_2 (extrapolated).

experimental angular momentum correlation times were obtained. Hard sphere diameters were calculated from the density dependent τ values and these diameters were used in a calculation, using Chandler's model, of the self-diffusion constants. The theoretical self-diffusion constants were in agreement with experimental values obtained from spin–echo measurements, when the hard sphere diameters were allowed to vary with temperature.

We have calculated theoretical rotational relaxation times for liquid CH_3I at 283.7 K for a wide range of τ_ω values using Eqs. (1) and (2). The results are given in Fig. 1. Experimental τ_1 (infrared) and τ_2 (Raman) single particle rotational relaxation times for methyl iodide have been reported by several authors.[5] Jones, Andersen, and Pecora reported τ_1 and τ_2 values of 3.1 ±0.4 and 1.5±0.4 ps, respectively, at 283.7 K. These values were obtained from the exponential part of the corresponding correlation functions. Zero-frequency relaxation times obtained from the experimental correlation functions of Jones *et al.* were the same as those obtained from the exponential part of the correlation functions within experimental uncertainty.[5,6] Theoretical τ_1 and τ_2 relaxation times in agreement with the experimental values can be obtained only for a very small value of τ_ω. For $\tau_\omega \simeq 2.5\times10^{-15}$ s, the plots in Fig. 1 yield τ_1 and τ_2 values of 2.9 and 1.6 ps, respectively. These theoretical rotational relaxation times seem to agree fairly well with the experimental values given above. However, such a small τ_ω value does not appear to be physically reasonable. Lyerla, Grant, and Wang reported an experimental angular momentum relaxation time for CH_3I of 0.12 ps,[7] which is a factor of 50 greater than the τ_ω obtained from Fig. 1. To investigate further, we used the $\tau_\omega = 2.5\times10^{-15}$ s value and various values of the molecular diameter d to calculate values for the packing fraction η, Enskog

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TABLE I. Parameters for CH_3I at 283.7 K using $\tau_\omega = 2.5 \times 10^{-15}$ s.

Molecular diameter d(Å)	Packing fraction η	Enskog relaxation time τ_E (s)	Roughness a[a]	Roughness for perfectly rough hard sphere[b]
3.5	0.22	6.3×10^{-13}	253	0.87
4.2	0.38	2.9×10^{-13}	116	0.90
4.8	0.56	8.7×10^{-14}	35	0.92
5.2	0.71	2.3×10^{-14}	9.3	0.93
5.55	0.87	2.4×10^{-15}	0.95	0.94
5.75	0.96	5.2×10^{-17}	0.021	0.95

[a] $a = \tau_E/\tau_\omega$. [b] $a = [(4I/md^2)+1]^{-1}$.

relaxation time τ_E, and roughness a. We also calculated the roughness of a perfectly rough hard sphere for the different diameters. The results are given in Table I. For diameters less than 5.5 Å, the a values calculated from τ_E and τ_ω are much larger than the roughness for the corresponding perfectly rough hard sphere. For physically reasonable roughness and diameter values, the packing fraction is much too great; e.g., for the most compact packing, face-centered cubic, $\eta = 0.74$.[8]

Thus, this small value of τ_ω, while giving τ_1 and τ_2 values in agreement with experimental results, is physically unreasonable. The theoretical τ_2 value for $\tau_\omega = 4\times10^{-12}$ s agrees with the experimental value, but the corresponding theoretical τ_1 value is a factor of 20 too small. We conclude that there is no physically acceptable value of τ_ω which can explain the experimental τ_1 and τ_2 data of methyl iodide. It would be interesting to use high pressure to investigate the density dependence of τ_1 and τ_2 in an attempt to learn more about the nature of molecular motion in liquids composed of nonspherical molecules.

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Barriers to internal rotation obtained by pseudopotential calculations

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In recent studies,[1–5] we have shown that the use of our molecular pseudopotential theory gives results that are comparable to those obtained with the same basis set in a full SCF calculation for all the molecular properties we have investigated. Here we describe the application of this method (the NOCOR procedure) to the calculation of barriers to molecular internal rotation.

The rotational barriers for a valence isoelectronic series—ethane, methylsilane, methylgermane, and methylstannane—are presented in Table I, in which the results of the NOCOR method are seen to compare well with those obtained by an equivalent full SCF calculation and with the best experimental values. Both the pseudopotential and the full SCF calculations were carried out in a minimum-Slater basis set, with each Slater orbital being expanded into a set of four Gaussian functions. The Slater exponents used in these calculations were molecularly optimized for ethane[7] and methylsilane.[8] For the two remaining molecules, the Slater exponents for the methyl hydrogens and the carbon atoms were chosen to be equal to those obtained for the methyl group in methylsilane. Atom-optimized Slater exponents were employed for the germanium and tin atoms, and their attached hydrogens were assumed to have an exponent of 1.0. On going from the staggered to the eclipsed

TABLE I. Comparison of total barriers to internal rotation computed by pseudopotential theory (NOCOR method), conventional self-consistent-field results, and experiment. All values in calories.

Molecule	NOCOR	SCF[a]	Experiment
C_2H_6	3010	3140	2928 ± 25[b]
CH_3SiH_3	1220	1520	1665 ± 50[c]
CH_3GeH_3	1330	1280	1239 ± 25[d]
CH_3SnH_3	690	···	650 ± 30[e]

[a] SCF values for the C_2H_6 and CH_3SiH_3 barriers have also been presented in Refs. 6–8.
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