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Raman scattering study of CS$_2$ in CCl$_4$

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Several spectroscopic techniques probe molecular reorientation in liquids. The most commonly used measurements are NMR, NQR, depolarized Rayleigh, and Raman light scattering. Depolarized Rayleigh light scattering is unique among these techniques in that it is a coherent process. The depolarized Rayleigh spectra reflect scattering from pairs of molecules. We reported recently results of the depolarized Rayleigh scattering study of CS$_2$ in an optically isotropic solvent, CCl$_4$.[1] The comparison of the CS$_2$ depolarized Rayleigh relaxation time data with that obtained using the ^{13}C-NMR and ^{33}S-NQR techniques suggests the presence of significant static orientational pair correlation (OPC) in the neat CS$_2$ liquid. The determination of the OPC factor by depolarized Rayleigh scattering is made according to[2]

$$\tau_{Ray} = \tau_s(1+fn)/(1+gn),\tag{1}$$

where τ_{Ray} is the Rayleigh relaxation time and τ_s is the single particle reorientational correlation time. n is the number density of scatterers and f and g are the static and dynamic OPC factors, respectively. τ_{Ray} is obtained from the depolarized Rayleigh spectrum according to $\tau_{Ray} = (2\pi\Delta\nu)^{-1}$ where $\Delta\nu$ is the half width at half height.

Recent calculations by Gierke based on symmetry arguments have shown that for linear and symmetric top molecules the dynamic OPC factor, g, is not present in the τ_{Ray} expression.[3] Gierke, however, assumes that the correlation of the angular velocities of different molecules is not related to their relative positions and orientations. Recently Wolynes and Deutch have determined a nonvanishing expression for g based on a hydrodynamic mechanism.[4] The applicability of their model to solutions of small molecules is open to question. Although experimentally[5-7,10] it is observed that g is negligibly small, one should not exclude this quantity in analyzing the depolarized Rayleigh spectra data.

The Raman relaxation time, τ_R, for a totally symmetric mode of a molecular liquid is obtained according to[8]

$$\tau_R^{-1} = \tau_{dep}^{-1} - \tau_{pol}^{-1},\tag{2}$$

where τ_{dep} and τ_{pol} are respectively the correlation times for the depolarized and polarized spectra. τ_{pol} for the polarized spectrum is corrected for the depolarized component.[8]

On the basis of the random phase approximation, it is commonly assumed that τ_R is equal to τ_s and Raman scattering reflects the dynamics of single particle molecular motion.[9] However, in the presence of intermolecular interactions, it is not certain that τ_R can be identified with τ_s. In addition, the validity of obtaining

single particle reorientation times from the polarized and depolarized spectral components according to Eq. (2) has been questioned by several authors.[9-11] Equation (2) assumes that the reorientational and vibrational contributions to the Raman linewidth are not coupled. While this assumption is not valid in CH$_2$Br$_2$[9] it has been shown to be valid in CH$_3$CN[12] and CH$_3$I[10] where Raman scattering probes single particle reorientation.

Since τ_s for CS$_2$ is accurately known by NMR,[13] NQR[13] and dilution depolarized Rayleigh scattering[1] experiments, it is useful to compare τ_R with τ_s in CS$_2$. We have carried out Raman scattering measurements of τ_R for CS$_2$ by analyzing the bandshape of the ν_1 symmetric stretch vibration which occurs at 656.6 cm^{-1}. A detailed description of the experimental set-up has previously been given.[12] The experimental spectra were acquired digitally and were corrected for the instrumental width. The digital spectra were fit to a Lorentzian function correcting for two less intense bands at slightly lower frequency.

The Raman relaxation times obtained in this manner from neat CS$_2$ as a function of temperature and from solutions of CS$_2$ in CCl$_4$ at 20 °C are plotted in Fig. 1 vs η/T. Also shown in Fig. 1 are the ^{13}C NMR and ^{33}S NQR relaxation times[13] as well as our recent infinite dilution depolarized Rayleigh relaxation times of Ref. 1. The excellent agreement between τ_R, τ_{NMR}, τ_{NQR}
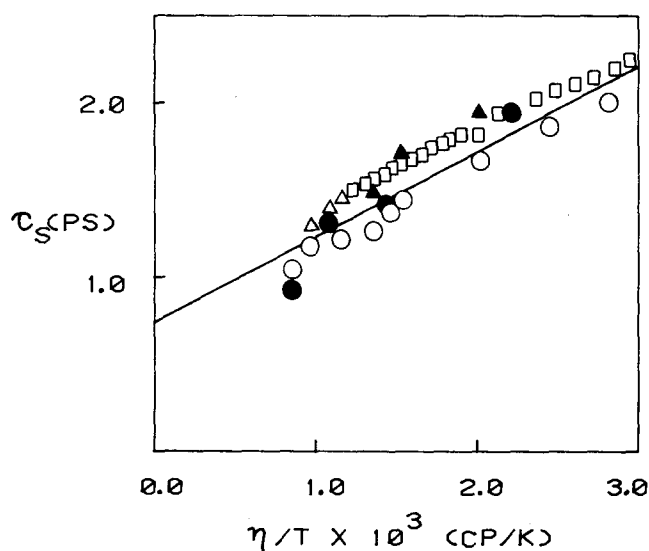

FIG. 1. Single particle time as a function of η/T; □ infinite dilution τ_{Ray}, ● ^{13}C magnetic resonance, ○ ^{33}S nuclear quadrupole resonance, △ τ_R neat CS$_2$ as a function of temperature, ▲ τ_R CS$_2$ as a function of concentration in CCl$_4$ at 20 °C.

and the infinite dilution τ_{Ray} strongly suggests that τ_R in the CS_2–CCl_4 system is a measure of τ_s.

The light scattering single particle reorientation time is a linear function of η/T. Therefore, the nonlinear relationship of the depolarized Rayleigh relaxation times with η/T reported in Ref. 1 arises because the OPC factor in CS_2 is a function of viscosity and temperature. At present there is no theoretical model predicting this viscosity and temperature dependence in the literature.

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On the use of contact potential difference measurements to determine isosteric heats of adsorption[a]

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The isosteric heat of adsorption of overlayers on solid surfaces is measured frequently at points of constant contact potential difference ($\Delta\phi$ or CPD).[1,2] However, both theory and experiment indicate the CPD for a fixed overlayer coverage (θ) may vary with temperature.[3] Here a method is developed for estimating the error in the isosteric heat by not including this effect.

If the partial molar volume of the adsorbed phase is small compared to that of the (ideal) gas phase, and if the surface area (a) does not vary upon chemisorption, the Clausius–Clapeyron relation for points of constant CPD may be written as

$$-\left[\frac{\partial \ln P}{\partial(1/T)}\right]_{\Delta\phi} = \frac{q_{st}}{k} + \frac{T}{k}\left(\frac{\partial \mu_s}{\partial \theta}\right)_{T_e, P, a}\left(\frac{\partial \theta}{\partial T}\right)_{\Delta\phi} \quad (1)$$

by equating the differential of the chemical potential of the adsorbed phase (μ_s) with that of the gas phase. In Eq. (1), P is the pressure in the gas phase, and q_{st} is the isosteric heat of adsorption. Equation (1) is the usual Clausius–Clapeyron relation[4] with an extra term, which is equal to the error (ϵ/k) introduced by ignoring the temperature variations of the CPD.

The quantity $(\partial\theta/\partial T)_{\Delta\phi}$ may be evaluated by assuming the Topping equation[5,6] relates the coverage and CPD at any temperature. A model will be adopted which assumes the CPD changes with temperature at any surface coverage by partitioning the admolecules between

two states of different electronic polarizabilities and permanent dipole moments.[3,7] The variation of the polarizability (α) and dipole moment (μ) with temperature allows the Topping equation to be written as

$$\left(\frac{\partial \theta}{\partial T}\right)_{\Delta\phi} = \frac{\theta}{T^2}\left(\frac{U}{4k}\right)\left[\frac{\Delta\mu}{\mu_R} + \theta\Lambda C_S^{3/2}\left(\frac{\Delta\mu}{\mu_R}\alpha_R - \Delta\alpha\right)\right] \quad (2)$$

where μ_R and α_R are the dipole moment and polarizability associated with the CPD at a fixed reference temperature; U is the height of an assumed periodic square well potential in the surface plane; $\Delta\mu$ is the magnitude of the difference of the permanent dipole moments for the minima and maxima of the potential; C_S is the concentration of adsites; and Λ is a (constant) structural parameter. At the reference temperature, the $\theta - \Delta\phi$ relation is established to give the coverage dependence of the isosteric heat. The error (ϵ) depends upon the choice of reference temperature (taken to be 300 K), as well as the coverage and temperature at which the Clausius–Clapeyron expression is evaluated.

For illustrative purposes, this model will be developed further for the particular case of CO chemisorption on the (110) surface of Ir.[3] Since the average surface electrical field for Ir(110) is the same for the two types of binding sites,[3] the second term in brackets in Eq. (2) vanishes. This should occur generally on metal surfaces if the dimension of the adsorbate is comparable to, or larger than, the dimension of the substrate unit

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