

## Models of the Orientational Autocorrelation Function from Far Infrared Absorption in Liquid and Rotator Phases

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Orientational time-autocorrelation functions derived from (i) a multi-site model, (ii) an itinerant oscillator model, and (iii) the  $J$ -diffusion model, of molecular motion in liquid and rotator phases are compared and contrasted in the 1 to 4 ps interval for symmetric top molecules. In contrast to the corresponding spectral bandshapes, these correlation functions are easily distinguishable, and yield information about the structuring of each phase.

The aim of this note is to compare time-autocorrelation functions of the dipole moment vector of some symmetric top, or nearly symmetric top, molecules calculated from the following models of molecular motion and interaction in condensed phases.

(1) The Brot-Larkin model<sup>1-4</sup> of the torsional oscillatory movement of a molecule whose rotation is constrained within potential wells generated by neighbouring molecules. The far infrared (3-200 cm<sup>-1</sup>) absorption predicted by this model has been compared<sup>5-7</sup> with experimental results for these molecules in the frequency domain. Here, this comparison is extended to the time domain.

(2) The Wyllie-Larkin<sup>1</sup> model of the "itinerant oscillator" which introduces non-spherical molecular potentials to the Debye model by invoking a relaxation of the cage of molecules within which a central one is situated. Optimum matches<sup>1, 5-7</sup> with experimental data have been obtained for many molecules of widely different geometries, but in the frequency domain (far infrared and microwave) only.

(3) The  $J$ -diffusion model<sup>8</sup> as extended by McClung<sup>9</sup> to symmetric top molecules. This assumes free rotation between instantaneous collisions separated by a time  $\tau$ . As  $\tau \rightarrow \infty$  the free rotor situation is approached, and as  $\tau \rightarrow 0$  a stochastic diffusion.

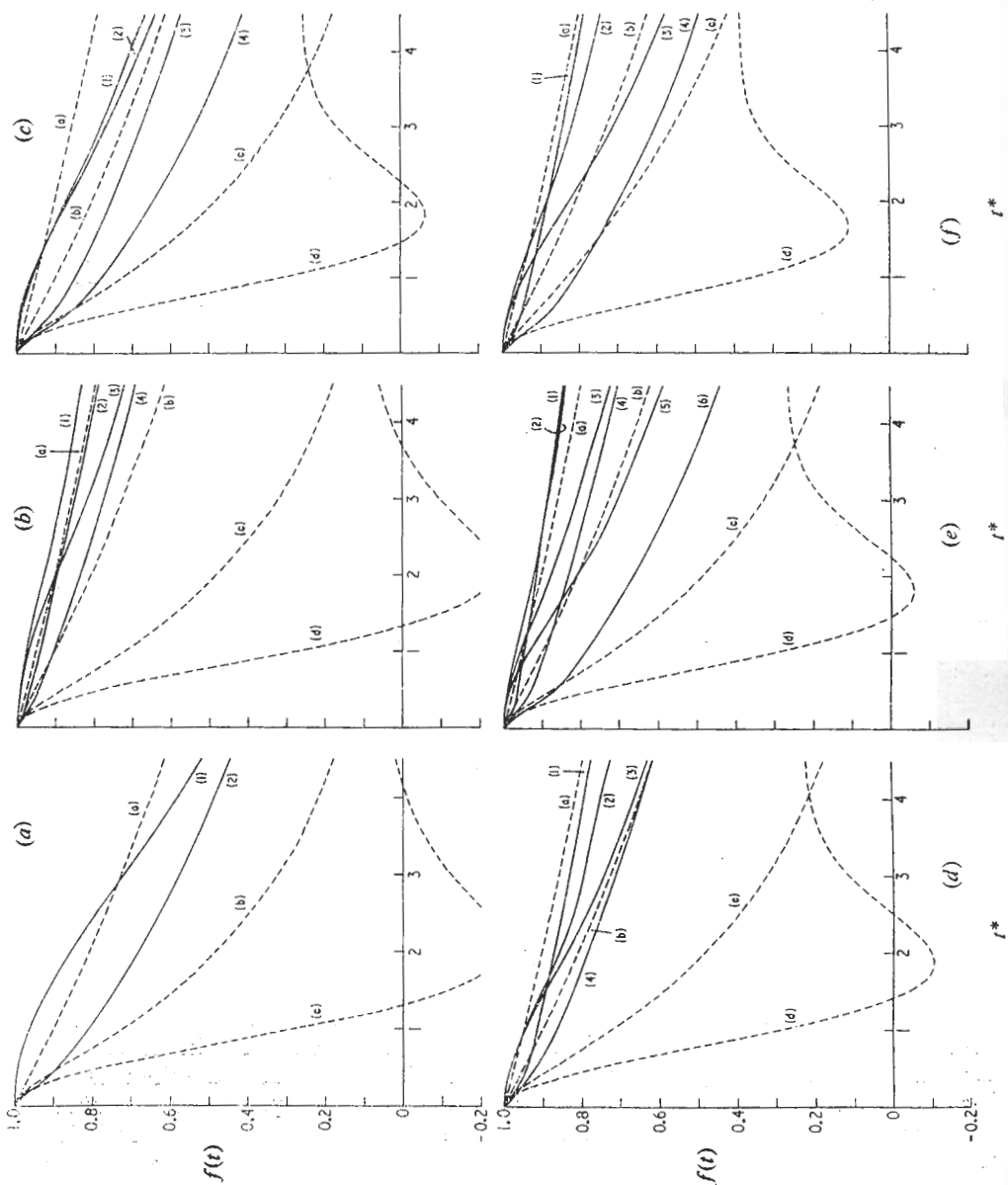
The computation of orientational autocorrelation functions:

$$f(t) = \frac{\langle \mathbf{u}(0) \cdot \mathbf{u}(t) \rangle}{\langle \mathbf{u}(0) \cdot \mathbf{u}(0) \rangle}$$

for each model exposes the differences between the models much more effectively<sup>3</sup> than a simple generation of the frequency domain curves. The differences are especially acute in the region 0-4 ps, since models (1) and (3) both use the ideas of hard collisions, when the intermolecular mean square torque becomes infinite theoretically. This has the consequence that the slope of the time-autocorrelation function cannot attain the Gordon value of zero as  $t \rightarrow 0$  (see fig. 1). Model (2), in contrast, is not a collisional-type and is well-behaved at short times.

### COMPUTATIONAL DETAILS

Orientational autocorrelation functions were computed for the molecules shown in the table, and are displayed in fig. 1. The  $J$ -diffusion functions were calculated for several values of  $\tau^* = \tau(kT/I)^{1/2}$ , the reduced mean time between collisions, using



double precision on a CDC 6600 computer with a program modified from one kindly supplied by Dr. R. E. D. McClung. The functions of model (1) were evaluated directly from an expression<sup>10</sup> given by Lassier and Brot. This contains several phenomenological parameters which Larkin *et al.*<sup>1-7</sup> have optimized by frequency domain curve fitting. The functions from model (2) were calculated by Fourier transformation of an expression given by Larkin<sup>1</sup> for the theoretical frequency dependent power absorption coefficient per unit path length of absorber [ $\alpha(\bar{\nu})$ ]. The algorithm involved integration by Simpson's rule of the real part of the Fourier integral in steps of  $10^{-3} \text{ cm}^{-1}$  from  $10^{-4} \text{ cm}^{-1}$  to about  $50 \text{ cm}^{-1}$  where further contributions from the integrand became negligible. The phenomenological parameters<sup>1</sup> were again those optimised by Larkin *et al.* as for model (1).

It is relevant to note that while the frequency domain curves<sup>1-7</sup> generated by models (1) and (2) often resemble each other closely, and are sometimes difficult to distinguish from the experimental data below  $3 \text{ cm}^{-1}$  and above  $20 \text{ cm}^{-1}$ , the time domain curves shown in fig. 1 are disparate and easily distinguishable. No experimental curves are shown because of the absence of data in the critical frequency range  $3\text{-}20 \text{ cm}^{-1}$ , a region investigable only with the help of He(I) cooled radiation detectors (solid state).

## DISCUSSION

The "gas-phase" free rotor curves ( $\tau^* \rightarrow \infty$ ) shown for each molecule reveal the extent to which rotational motion is constrained in the liquid and "rotator" phases. Although models (1) and (2) give an imperfect representation of the "true" situation, they can probably be taken as extremes within which the experimental autocorrelation function would fall if data in the region  $3\text{-}20 \text{ cm}^{-1}$  were available at a given temperature and in a given phase.† The  $J$ -diffusion model then requires reduced times ( $\tau^*$ ) between adiabatic collisions of  $\sim 0.01\text{-}0.05$  to match models (1) and (2).

FIG. 1.—(a) Orientational autocorrelation functions for liquid propyne<sup>11</sup> at 296 K. — (1) Wyllie-Larkin model, (2) Brot-Larkin model; - - - (a) McClung  $J$ -diffusion model with  $\tau^* = 0.05$ , (b)  $\tau^* = 0.20$ , (c) free rotor.

FIG. 1.—(b) Orientational autocorrelation functions for liquid dichloromethane. — (1) Wyllie-Larkin model at 188 K, (2) Brot-Larkin model at 188 K, (3) Wyllie-Larkin model at 298 K, (4) Brot-Larkin model at 298 K. - - - (a) McClung  $J$ -diffusion model with  $\tau^* = 0.01$ , (b)  $\tau^* = 0.05$ , (c)  $\tau^* = 0.20$ , (d) free rotor.

FIG. 1.—(c) Orientational autocorrelation functions for t-butylchloride. — (1) Wyllie-Larkin model at 238 K (rotator phase), (2) Wyllie-Larkin model at 274 K (liquid phase), (3) Brot-Larkin model at 238 K, (4) Brot-Larkin model at 274 K. - - - (a) McClung  $J$ -diffusion model with  $\tau^* = 0.01$ , (b)  $\tau^* = 0.05$ , (c)  $\tau^* = 0.20$ , (d) free rotor.

FIG. 1.—(d) Orientational correlation functions for 2-methyl-2-nitropropane [(CH<sub>3</sub>)<sub>3</sub>CNO<sub>2</sub>]. — (1) Brot-Larkin model at 273 K (rotator phase), (2) Wyllie-Larkin model at 273 K, (3) Wyllie-Larkin model at 294 K (liquid phase), (4) Brot-Larkin model at 294 K. - - - (a) McClung  $J$ -diffusion model with  $\tau^* = 0.01$ , (b)  $\tau^* = 0.05$ , (c)  $\tau^* = 0.20$ , (d) free rotor.

FIG. 1.—(e) Orientational autocorrelation functions for 2,2-dichloropropane [(CH<sub>3</sub>)<sub>2</sub>CCl<sub>2</sub>]. — (1) Brot-Larkin model at 192 K (rotator phase), (2) Wyllie-Larkin model at 192 K, (3) Wyllie-Larkin model at 241 K (rotator phase), (4) Brot-Larkin model at 241 K, (5) Wyllie-Larkin model at 295 K (liquid phase), (6) Brot-Larkin model at 295 K (liquid phase). - - - (a) McClung  $J$ -diffusion model with  $\tau^* = 0.01$ , (b)  $\tau^* = 0.05$ , (c)  $\tau^* = 0.20$ , (d) free rotor.

FIG. 1.—(f) Orientational autocorrelation functions for 2,2-dichloropropane. — (1) Brot-Larkin model at 233 K (rotator phase), (2) Wyllie-Larkin model at 233 K, (3) Wyllie-Larkin model at 293 K (liquid phase), (4) Brot-Larkin model at 293 K. - - - (a) McClung  $J$ -diffusion model with  $\tau^* = 0.01$ , (b)  $\tau^* = 0.05$ , (c)  $\tau^* = 0.10$ , (d) free rotor.

† It is not possible to modify arbitrarily the parameters in models (1) and (2) to give similar correlation functions, because of their in-built<sup>12</sup> short-time differences.

In the translationally invariate rotator phase, this implies that rotation through very small angles only is possible before "collision" randomizes the angular momentum of the molecule in both magnitude and direction. Slightly larger values of  $\tau^*$  are predicted by this model in the liquid phase than in the rotator phase [fig. 1(c)-(f)] but these are still low enough to indicate that the average duration of a period of free rotation is much shorter than the average time needed for rotation of the molecule through  $2\pi$  radians. The molecules translate by less than their van der Waals radius between collisions, so that rotational motion alone is sufficient to cause molecular interactions.

TABLE I.—ROTATIONAL CONSTANTS FOR THE MOLECULES STUDIED

molecule	temperature/K	$A/\text{cm}^{-1}$	$B/\text{cm}^{-1}$	$C/\text{cm}^{-1}$
$\text{CH}_3\text{C}\equiv\text{CH}$	295	5.100	0.285 2	0.285 2
$(\text{CH}_3)_3\text{CCl}$	238, 274	0.177	0.100 6	0.100 6
$(\text{CH}_3)_3\text{CNO}_2$	273, 294	0.177	0.076	0.076
$\text{CH}_3\text{CCl}_3$	233, 293	0.056	0.080	0.080
$\text{CH}_2\text{Cl}_2^*$	188, 249, 298			
$(\text{CH}_3)_2\text{CCl}_2^*$	192, 241, 295			

\* Approximate symmetric tops.

The smaller  $\tau^*$  in the rotator phase <sup>6</sup> reflects the structuring where a rotating central molecule has to regularly surmount potential energy barriers <sup>6</sup> of about  $kT$  or a few  $kT$  arising from the averaged resultant fields of neighbouring molecules. In the liquid, translational motion is simultaneously taking place with rotational motion, creating some "free volume" so that potential barriers are encountered less often over a sufficiently extended period of time.

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