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RISE TRANSIENT DYNAMICS OF SUPERCOOLED sec-BUTYL CHLORIDE - a COMPUTER SIMULATION

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ABSTRACT

The role of chiral discrimination in the R enantiomer and racemic mixture of sec butyl chloride is investigated by computer simulation in the glassy condition at 50K. The effect of left or right handedness on the molecular dynamics is clearly measurable at equilibrium in the appropriate frame of reference. The physical (lab. frame) effects of chiral discrimination are emphasized by the application of a strong, external electric field. This produces deeply oscillatory rise transients whose time dependence is clearly different for enantiomer and racemic mixture at the same nominal temperature (50K).

INTRODUCTION

The molecular dynamics of chiral molecules in the liquid and disordered solid states of matter depend on the difference between the potential energy of interaction of left and right handed stereo isomers [1]. This is known usually as chiral discrimination [2]. It is known [3] that small difference in interaction energy (R - R, S - S; and R - S etc.) can result in measurable differences on a macroscopic level, manifested, for example, in the melting point or boiling point and certain spectroscopic properties [4]. Recently it has been shown by computer simulation [5,6] that chiral discrimination appears clearly in a moving frame cross-correlation matrix such as $\langle \underline{v}(t)\underline{J}^T(o)\rangle_m$, where $\underline{v}$ is the chiral molecule's centre of mass velocity and $\underline{J}$ its angular momentum in a moving frame of reference defined conveniently as that of the principal moments of inertia. In this case well-defined elements of $\langle \underline{v}(t)\underline{J}^T(o)\rangle_m$ are antisymmetric in their time dependence. These same elements vanish for all t for the racemic mixture. This is a molecular dynamical origin of differences in physical properties (such as spectra) between the R (or S) enantiomer and solutions of enantiomers such as the

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racemic mixture. By applying an intense electric field to S-CHBrClF in a computer simulation it was shown further that elements of $<\underline{v}(t)\underline{J}^T(o)>_m$ become observable directly in the laboratory frame and that the electric field produces translation in a well-defined direction in the laboratory frame [7,8]

In this letter we extend these investigations to the case of sec butyl chloride in the glassy or supercooled condition where chiral discrimination plays an important role in determining the physical and chemical properties of the bulk system. There is a well-defined and accurately measured difference [9] in the melting points of either enantiomer and their racemic mixture. This produces the molecular dynamical problem of why two liquids, with seemingly identical physical properties (such as zero-THz profiles) should solidify on mixing in the range between the melting points of enantiomers and racemic mixture. This cannot be solved without adequate consideration [6] of cross-correlations exemplified by $<\underline{v}(t)\underline{J}(o)^T>_m$. We aim to look at these with computer simulation with and without an applied field. Under these conditions the molecular dynamical effect of the chiral discrimination between molecular potential energies can be observed clearly.

ALGORITHM AND METHOD

This is a development of an algorithm designed for polyatomics [10]. The molecular dynamics of each enantiomer are simulated at 50K in the supercooled state with 108 sec butyl chloride molecules and those of the racemic mixture with 54 molecules each of R and S stereo isomer. Chiral discrimination is built into the system by using a site-site model [11] for the pair interaction potential consisting of atom-atom Lennard Jones terms and partial charges. In this way the space-averaged pair-interaction energy should be slightly different [1] for R-R (or S-S) pairs and R-S pairs. By partially locking the molecules into a glass well below the normal melting points we can emphasize the chiral discrimination by partially removing spatial isotropy. It is well known that the infra-red spectrum, for example, of enantiomers and racemic mixture in the solid state can be very different in appearance [12,13] reflecting the differences in structure and dynamics. The electric field treatment, using methods developed elsewhere [14] for non-chiral molecular symmetries, provides us with an additional powerful means of measuring the effects of chiral discrimination on a pairwise molecular level.

Differences in the molecular dynamics of the R sec butyl chloride enantiomer and the racemic mixture are monitored with fixed and moving frame [15] correlation functions and with transient averages over orientation and centre of mass velocity components in the laboratory frame, with and without the use of a powerful, external, electric field.

RESULT AND DISCUSSION

The chiral determination in elements of the moving frame matrix $\langle \underline{v}(t)\underline{J}^T(o)\rangle_m$ is illustrated in fig. (1). Analytical theories have still to be

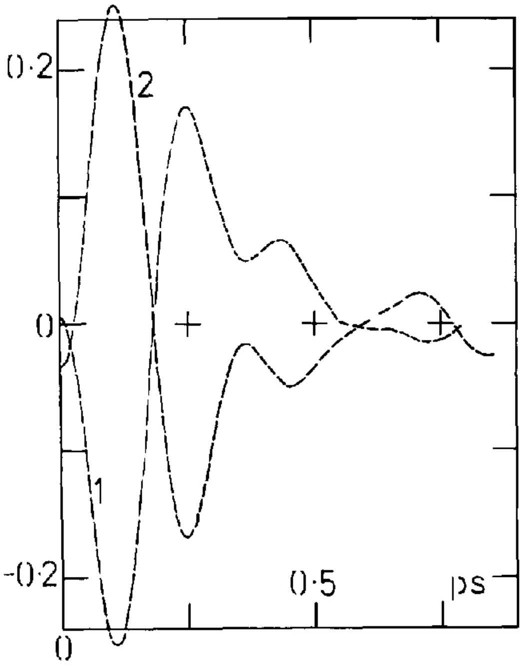

Fig. 1. (1) (1,3) element of the moving frame matrix correlation function $\langle \underline{v}(t)\underline{J}^T(o)\rangle_m$. The (1.3) element is defined by $\langle v_1(t)J_3(o)\rangle/[\langle v_1^2\rangle^{\frac{1}{2}}\langle J_3^2\rangle^{\frac{1}{2}}]$
(2) (3,1) element in the same moving frame.
Abscissa: time/ps.

developed to account for these differences and to describe related laboratory frame autocorrelation functions ($\langle \underline{v}(t).\underline{v}(o)\rangle$ and $\langle \underline{J}(t).\underline{J}(o)\rangle$) self-consistently. Work on these lines is in progress, using the RMT structure developed by Grigolini [16,17,18]. In the laboratory frame the autocorrelation functions of $\underline{v}$ and $\underline{J}$ are oscillatory (fig. (2)), and describe the residual thermal motion in the glassy phase of racemic and enantiomeric

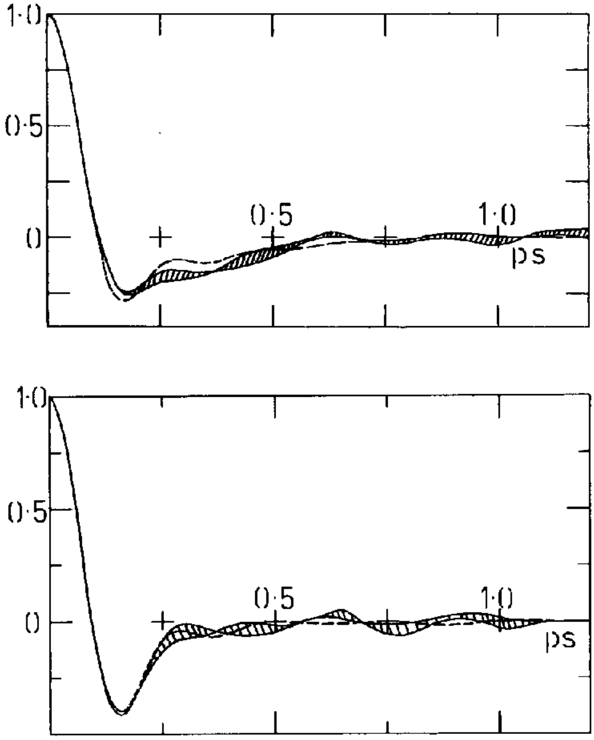

Fig. 2. Equilibrium autocorrelation functions
(a) - - - Centre of mass a.c.f. $\langle \underline{v}(t).\underline{v}(o)\rangle/\langle v^2\rangle$, racemic mixture. The same for R and S enantiomers. The hatched area indicates the noise in the simulation.
(b) As for (a), angular momentum auto correlation functions.
Abscissa: time/ps.

sec butyl chloride at 50K, supercooled below the normal melting points [9] of mixture and component respectively.

The application of a strong, external, electric field produces transient behaviour such as that illustrated in fig. (3). These transients are built up of the orientational averages [14] $\langle e_{3z}\rangle_{108}$ for the racemic mixture and R enantiomer. Here e_{3z} is the laboratory frame Z component of $\underline{e}_3$, a unit vector in the 3 axis of the principal molecular moment of inertia tensor. There are two interesting and original features in fig. (3).

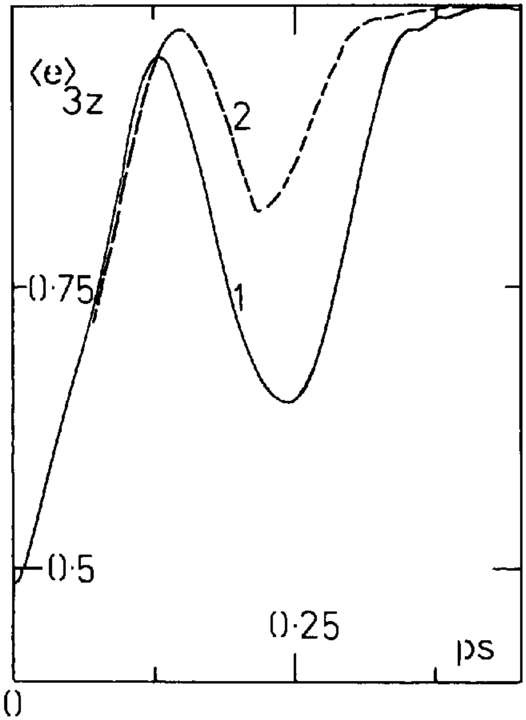

Fig. 3. Rise transients $<e_{3z}>_{108}$ for:
(1) Racemic mixture; (2) R enantiomer.
The transients are oscillatory and have a different time dependence for enantiomer and racemic mixture - due to chiral discrimination on the single molecule level.
Abscissa: time/ps.

i) The time dependence of each rise transient is different, i.e. there is a clear lab. frame difference between the dynamics of enantiomer and racemic mixture. This provides us, in principle, with a means of evaluating the cross-correlations $<\underline{v}(t)\underline{J}^T(o)>_m$ by comparison of rise-transients [6].

ii) The rise transients are oscillatory in both cases, and more so in the racemic mixture. Deep oscillations such as these have been predicted theoretically by Coffey, Rybarsch and Schroer [19] using an external cosine potential superimposed on Brownian motion in an ensemble of particles.

The external electric field used to produce the results of fig. (3) is strong enough to saturate the transient. This reveals some properties of the molecular dynamical ensemble which are otherwise difficult to find and describe quantitatively. The computer simulation may be used to supplement the elegant analytical methods developed by Morita et al. [20], Coffey et al. [21], and Grigolini et al. [22] when these run up against purely technical difficulties caused by mathematical complexity. In this context it is necessary to note that electromagnetic field strengths currently available should produce oscillatory rise transients such as those in fig. (3).

ACKNOWLEDGEMENTS

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