Intermolecular Coriolis and Centrifugal Forces in Chiral Molecules: Laboratory-Frame Differences between Enantiomers and Racemic Mixtures

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The first computer simulation of the time-correlation functions of the intermolecular Coriolis and centrifugal forces reveals that these functions are different in the laboratory frame for (R)- and (S)-CHBrClF and the racemic mixture. This (observable) laboratory-frame difference is due to the differential statistical interdependence in this frame of a molecule's rotation on its own translation in enantiomers and mixture.

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The molecule-fixed frame is a noninertial frame of reference[1] with respect to the laboratory frame and vice-versa. If the frame is defined as the frame of principal molecular moments of inertia, then the angular velocity, $\boldsymbol{\omega}$, of a diffusing molecule is also the angular velocity of one frame compared with the other. Therefore for each molecule in the ensemble, there exist in the laboratory frame the Coriolis force $2m\mathbf{v}\times\boldsymbol{\omega}$ and centrifugal force $m\boldsymbol{\omega}\times(\boldsymbol{\omega}\times\mathbf{r})$, together with the force $m\mathbf{r}\times\dot{\boldsymbol{\omega}}$ due to the nonuniformity of the angular velocity of one frame with respect to the other.[1] Here $\mathbf{v}$ is the linear center of mass of the molecule, $\mathbf{r}$ is the position of this center of mass in the laboratory frame at an instant t, and m is the molecular mass. These three forces are natural measures of the statistical interdependence of the vectors $\mathbf{r}$, $\mathbf{v}$, and $\boldsymbol{\omega}$ in molecular ensembles because they arise directly[1] from Newton's equation written in a noninertial frame of reference—the laboratory frame itself. It follows that time correlations of these three forces exist in the laboratory frame, and provide statistical information on this interdependence. The Fourier transforms of these three types of correlation functions are laboratory-frame spectra,[2] whose frequency dependence is determined directly by the relevant cross products among the vectors $\mathbf{r}$, $\mathbf{v}$, and $\boldsymbol{\omega}$ (see Appendix).

This Letter computes these laboratory-frame correlation functions for the first time, and shows that they are different in an enantiomer and racemic mixture of a chiral molecule,[3,4] in this case bromochlorofluoromethane (CHBrClF). It follows conversely that a comparison of experimental spectra for, say, (R)-CHBrClF and its racemic mixture provides information directly on the statistical interdependence of $\mathbf{r}$, $\mathbf{v}$, and $\boldsymbol{\omega}$.

As far as we are aware, these autocorrelation functions (ACF's) have never been considered explicitly in theories of molecular diffusion based on stochastic equations of motion.[2,5] This Letter establishes beyond doubt that these ACF's nevertheless exist, and are an intrinsic part of the statistics of the molecular-diffusion process in the molecular liquid and similar states of matter.

Computer simulation method.—The technique of constant-volume "molecular dynamics" computer simulation[6] was used (i) for 108 (R)-CHBrClF molecules, and (ii) 54 molecules each of (R)- and (S)-CHBrClF—the racemic mixture. The input temperature was 296 K and input molar volume 1.20×10^{26} Å^3/mol. The intermolecular pair potential was modeled with a 5×5 site-site sum, each site consisting of the following atom-atom Lennard-Jones parameters for repulsion and dispersion, and partial point charges for electrostatics:

$$\epsilon/k(\text{C-C}) = 35.8\ \text{K}, \quad \sigma(\text{C-C}) = 3.4\ \text{Å}, \quad q_{\text{C}} = 0.335|e|,$$
$$\epsilon/k(\text{H-H}) = 10.0\ \text{K}, \quad \sigma(\text{H-H}) = 2.8\ \text{Å}, \quad q_{\text{H}} = 0.225|e|,$$
$$\epsilon/k(\text{Br-Br}) = 218.0\ \text{K}, \quad \sigma(\text{Br-Br}) = 3.9\ \text{Å}, \quad q_{\text{Br}} = -0.160|e|,$$
$$\epsilon/k(\text{Cl-Cl}) = 158.0\ \text{K}, \quad \sigma(\text{Cl-Cl} = 3.6\ \text{Å}, \quad q_{\text{Cl}} = -0.180|e|,$$
$$\epsilon/k(\text{F-F}) = 54.9\ \text{K}, \quad \sigma(\text{F-F}) = 2.7\ \text{Å}, \quad q_{\text{F}} = -0.220|e|.$$

These parameters were taken from the literature[7,8] and assumed to be the same for both R-R intermolecular pair potentials and R-S interactions. There are no experimental indications to the contrary because the true pair potential is unknown. However, there is, probably, a small effect of chiral discrimination,[3] so that each R-R atom-atom potential is about 0.1% different on average from the equivalent R-S potential. The effect of chiral discrimination at equilibrium is too small to account for the large dynamical effects reported here for the first time directly in the laboratory frame.

After equilibration, the correlation functions of $2m\mathbf{v}\times\boldsymbol{\omega}$ were evaluated with running time averages[2] in the usual way, using 1000 time steps (500 records separated by 0.01 ps). These are described in the next section for the enantiomer and mixture.

Figures 1–3 compare for (R)- and (S)-CHBrClF and their racemic mixture the normalized ACF's:

$$C_{\mathrm{Cor}}=\frac{\langle \mathbf{v}(t)\boldsymbol{\omega}(t)\cdot\mathbf{v}(0)\times\boldsymbol{\omega}(0)\rangle}{\langle[\mathbf{v}(0)\times\boldsymbol{\omega}(0)]^2\rangle}, \tag{1}$$

$$C_{\mathrm{cent}}=\frac{\langle\{\boldsymbol{\omega}(t)\times[\boldsymbol{\omega}(t)\times\mathbf{r}(t)]\}\cdot\{\boldsymbol{\omega}(0)\times[\boldsymbol{\omega}(0)\times\mathbf{r}(0)]\}\rangle}{\langle\{\boldsymbol{\omega}(0)\times[\boldsymbol{\omega}(0)\times\mathbf{r}(0)]\}^2\rangle}, \tag{2}$$

$$C_T=\frac{\langle[\mathbf{r}(t)\times\dot{\boldsymbol{\omega}}(t)]\cdot[\mathbf{r}(0)\times\dot{\boldsymbol{\omega}}(0)]\rangle}{\langle[\mathbf{r}(0)\times\dot{\boldsymbol{\omega}}(0)]^2\rangle}. \tag{3}$$

The first and third of these functions vanish as $t\to\infty$, but C_{cent} reaches a plateau level which is different (Fig. 2) for enantiomer and mixture. (It is straightforward to take Fourier transforms of C_{cor} and C_T. The spectra peak at different frequencies for enantiomer and mixture.) These figures show conversely that such comparisons give direct information on molecular forces that involve **v**, **ω**, and **r** explicitly. Note carefully that C_{cor}, C_{cent}, and C_T have no existence in theories of uncoupled "rotational" and "translational" diffusion,[2,5] but are, nevertheless, basic to the molecular dynamics because they come directly from Newton's equation, written for a noninertial frame of reference.[1] Figures 1–3 illustrate these time-correlation functions for the first time, as far as we are aware, for any liquid or molecular material.

It is known already[7,9] that **v** and **ω** correlate differently in the principal molecular moment-of-inertia frame for enantiomer and mixture. This is, of course, the moving frame of reference in which no direct laboratory-frame observations can be made. This Letter provides for the first time the critically important link between moving-frame rototranslational time-correlation functions such as $\langle\mathbf{v}(t)\boldsymbol{\omega}^T(0)\rangle_m$ and the laboratory-frame rototranslational correlation functions C_{cor}, C_{cent}, and C_T. The difference between enantiomer and mixture shows up in the moving frame in only two (off-diagonal) elements of the matrix $\langle\mathbf{v}(t)\boldsymbol{\omega}^T(0)\rangle_m$. These two elements are correlation functions which are mirror images in time dependence for the R and S enantiomers and cancel to zero for all t in their racemic mixture.[7,9,10] The symmetry of the matrix $\langle\mathbf{v}(t)\boldsymbol{\omega}^T(0)\rangle_m$ is therefore wholly different[10] for enantiomer and mixture. It is precisely this difference which works its way through into the laboratory frame and therefore becomes directly observable in Fig. 1, and a little more indirectly in Figs. 2, 3, and 4.

Known spectra, such as far-infrared power absorption [Fig. (4)], are Fourier transforms, essentially[2] of time-correlation functions such as $\langle\dot{\boldsymbol{\mu}}(t)\cdot\dot{\boldsymbol{\mu}}(0)\rangle$ where $\boldsymbol{\mu}$ is the molecular dipole moment. The behavior of correlation functions such as these is governed by the same equations of motion as those of the functions computed in this Letter. Therefore, it seems that computer simulation is the only available method at present for describing these spectra fully, properly, and self-consistently in terms of both molecular rotation and translation. The stochastic theory of "uncoupled" molecular diffusion[2,5] is clearly in trouble if Figs. 1–3 are to be considered at all. The most promising escape route at the moment seems to be via the powerful and (in its own context) self-consistent reduced-model theory of Grigolini.[11]

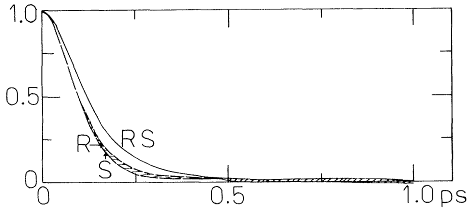

FIG. 1. Comparison of the intermolecular Coriolis force time correlation for (dashed curves) the R and S enantiomers, and (solid curve) the racemic mixture of liquid CHBrClF at 296 K. Noise level in RS.

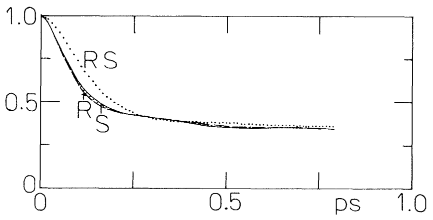

FIG. 2. As for Fig. 1, centrifugal forces.

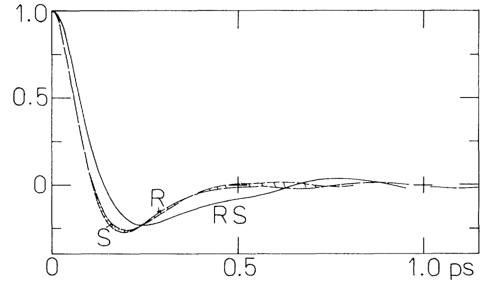

FIG. 3. Comparison of time-correlation functions for the force $m\dot{\boldsymbol{\omega}} \times \mathbf{r}$ due to the nonuniformity of the molecular angular motion (see text).

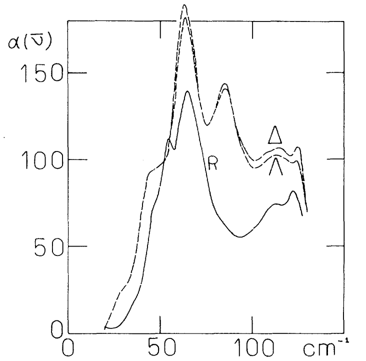

FIG. 4. Dashed curves, far-infrared power absorption of the Δ and Λ enantiomers of the cobalt tri(acetylacetonate) complex as pressed disks of the powdered solid. There is a lattice mode at 84 cm^{-1} which disappears in the racemic mixture. Solid curve, power absorption of the racemic mixture under the same conditions. The power-absorption coefficient is $\alpha(\bar{\nu})$ in nepers per centimeter.

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Appendix: Experimental corroboration for the computer simulation results.—It is clear from the text that statistical correlations between **v**, **ω**, and **r** exist in the laboratory (and moving) frames of reference, and influence observable spectra through the fundamental equations of motion. Conversely, these spectra provide information on this type of statistical correlation through the intermediary of computer simulation. In this Appendix an example of such a spectrum is provided for the Δ and Λ enantiomers and racemic mixture of the cobalt acetylacetonate complex $\text{Co}^{\text{III}}(\text{AcAc})_3$ in the powdered solid state. In Fig. 4 the far-infrared phonon modes of powdered disks of the two enantiomers and the racemic mixture are shown in the region up to 150 cm^{-1}. These power-absorption spectra were obtained with a Grubb-Parsons/National Physical Laboratory interferometer using three carefully weighed and prepared disks of exactly the same thickness. It can be seen that the phonon mode at 85 cm^{-1} for each enantiomer disappears in the racemic mixture, and that the peak at 65 cm^{-1} is reduced in intensity in the mixture. The precision of these experimental results can be estimated through the fact that the experimental spectra for the Δ and Λ enantiomers are, as they should be, almost exactly the same on the scale of Fig. 4. The Fourier transform of the phonon mode at 85 cm^{-1} in the enantiomers is a rotational-velocity autocorrelation function of time, which can, in principle, be built up by computer simulation. The *same* simulation run could be used to produce Coriolis and centripetal ACF's and so on as in the text. It is clear that this phonon mode has vanished in the racemic mixture. *The only possible dynamical difference between two enantiomers* is to be found[9] in the cross-correlation $\langle \mathbf{v}(t)\boldsymbol{\omega}^T(0)\rangle_m$ of the frame (1,2,3). This is the only possible reason, *in terms of time-correlation functions,* why a mixture of two enantiomers, whose spectra in the laboratory frame are identical (Fig. 4), should give a *different* spectrum when mixed in equal proportion. Therefore Fig. 4 provides information on statistical correlations between **v** and **ω**.

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