

DIRECT OBSERVATION OF MOLECULAR ROTATION-TRANSLATION COUPLING BY FAR-INFRARED SPECTROSCOPY

G.J. EVANS and M.W. EVANS

Edward Davies Chemical Laboratories, University College of Wales, Aberystwyth SY23 1NE, UK

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The differences between the far-infrared absorption of liquid (+)3-methylcyclohexanone and the racemic mixture are interpreted as supporting evidence for the direct observation of rotation-translation coupling.

In a recent study, one of us observed a new and unexpected phenomenon of the liquid state [1]. For the first time in a computer simulation, the effect of a molecule's rotation on its own translation was observed in the laboratory frame in the optically active molecule 1,1-fluorochloroethane. It was suggested that this phenomenon should be observable by several different spectroscopic techniques.

The simulation was carried out with a 5×5 atom-atom Lennard-Jones potential with partial charges [2] at each site designed to represent electrodynamic interactions. Dynamical data were stored on disk for the computation of autocorrelation functions using running time averaging. A variety of autocorrelation functions of various vectors associated with the molecular motion were produced. Fourier transformation of appropriate autocorrelation functions (ACFs) produces spectra. In particular Fourier transformation of the rotational velocity ACF provides a far-infrared spectrum [3].

The simulation revealed that the orientational autocorrelation functions of the P_1 and P_2 Legendre polynomials (the first is obtained from the far-infrared spectrum) were the same for the R and S enantiomers but different for the racemic mixture. This was a consequence of the fact that two elements of the molecular rotating frame matrix $\langle \mathbf{v}(t) \cdot \mathbf{J}^T(0) \rangle$ are opposite in sign for each enantiomer (this does not show up as a difference in the spectra) and vanish in the racemic, this being the only observable dynamical difference in the simulation. Here \mathbf{v} is the centre-of-mass velocity and \mathbf{J} the angular momentum. The effect is directly attribut-

able, therefore, to the interaction of rotation with translation and was so large in this particular liquid that the far-infrared spectrum was shifted from $\approx 35 \text{ cm}^{-1}$ in the enantiomers to $\approx 65 \text{ cm}^{-1}$ in the racemic mixture (the Debye loss time was approximately halved). This effect is as large as any shifts observed in the far infrared, including dilution of a solute in a non-polar solvent or the effects of temperature and externally applied pressure, and reveals a considerable difference in the molecular dynamics.

In a molecule now being simulated, 1,1-fluoroiodoethane, the effects are not so pronounced and only a small shift in $\bar{\nu}_{\text{max}}$ (the far-infrared peak frequency) is found which may even be in the opposite direction. These results will be presented in a later publication.

The R and S enantiomers of the 1,1-fluorochloroethane and the 1,1-fluoroiodoethane have not been isolated, so we have chosen (+)3-methylcyclohexanone (a naturally occurring product) and its racemic mixture. The two spectra are shown in fig. 1. There is a marked difference between the spectra, certainly in intensity. There is also a suggestion of a difference in the frequency of maximum absorption of the broad band at the lowest frequency of the enantiomer and racemic mixture. This is the so called "Poley" absorption characteristic of all molecular liquids at far-infrared frequencies. The intensity differences are displayed more clearly in fig. 2 where the integral transmission [the transmitted power over a complete frequency range ($50\text{--}250 \text{ cm}^{-1}$ in this instance)] has been monitored for changes in sample thickness. The racemic mixture is considerably more absorbing than the enantiomer even though the

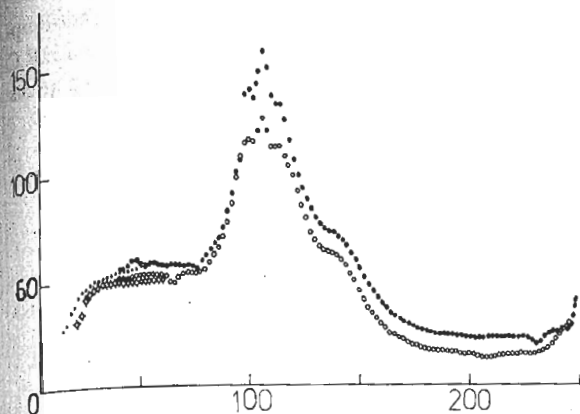


Fig. 1. The far-infrared spectra of (+)3-methylcyclohexanone and a racemic mixture of 3-methylcyclohexanone. *, results for the racemic mixture using a 200 gauge beam divider; •, results for the racemic mixture using a 35 gauge beam divider; +, results for the enantiomer using a 200 gauge beam divider; o, results for the enantiomer using a 35 gauge beam divider. Ordinate: $\alpha(\nu)$ (neper cm^{-1}), abscissae: wavenumber (cm^{-1}).

densities of both liquids are the same (to the third decimal place in g/cm^3). The origin of the absorption (at $\approx 110 \text{ cm}^{-1}$), composed of a series of absorptions, will be the subject of a future discussion.

The beam from our spectrometer (a Grubb-Parsons/NPL cube interferometer) is partly polarized,

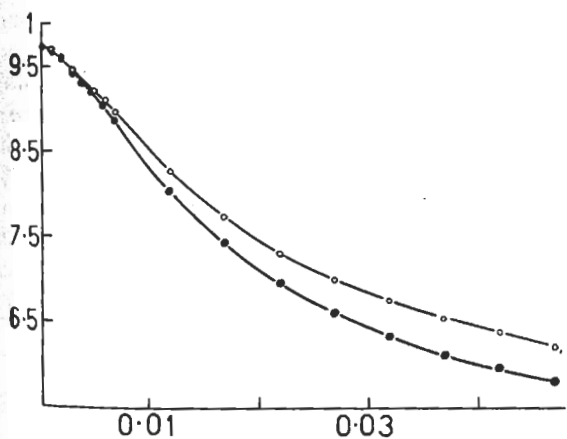


Fig. 2. Variation of the integral transmission ($50\text{--}250 \text{ cm}^{-1}$) with pathlength of (+)3-methylcyclohexanone and a racemic mixture. •, racemic mixture, o, (+)3-methylcyclohexanone. Ordinate: volts, abscissae: pathlength (cm).

a consequence of the beam splitters (Melinex) used in the instrument. Results using completely polarized radiation indicate the same differences in spectral intensity between enantiomer and racemic mixture so that these spectral differences may only be attributed to *dynamical differences* between enantiomer and racemic mixture.

We believe that the results presented here provide support for the simulation. This is significant because together they reveal a profound influence of rotation-translation coupling on the molecular dynamics of *all molecular liquids*. Simulations on optically inactive molecular liquids have indicated the existence of rotation-translation interaction in most liquids which may be very strong in some ($\text{CH}_3\text{CN}^\ddagger$). However, the effects of this interaction are normally concealed in the laboratory frame because a molecule such as CH_3CN is not optically active. The parity of \mathbf{v} is different to that of \mathbf{J} and autocorrelation functions such as $\langle \mathbf{v}(t) \cdot \mathbf{J}(0) \rangle$ must vanish (note however, that $\langle \mathbf{v}^2(t) \mathbf{J}^2(0) \rangle$ exists in the laboratory frame). The effects of the interaction are only observed directly in a rotating frame of reference in these systems. In an optically active system the effect of this interaction on an *orientational* autocorrelation function may be observed directly through the spectral differences between the enantiomer and its racemic mixture. Computer simulation reveals that this difference arises from differences in the rotation-translation interaction.

The authors know of one other direct observation of the large effects of rotation-translation interaction. Ewing et al. [7] reported spectra for dilute solutions of H_2 , D_2 and HD in liquid argon in which the rotational and translational transitions are easily distinguished and where the complications of interpreting a broad and featureless spectral profile are removed. For H_2 and D_2 the frequencies of the rotational transitions do not differ from those calculated for the unperturbed gas-phase molecule. However, the far-infrared spectrum of HD in liquid argon shows much larger half-widths, erratic frequency shifts, and additional absorptions arising from the relaxation of rotational selection rules. These anomalous characteristics are explained by a consideration of rotation-translation coupling when transitions corresponding to $\Delta J = +2, +3$ and $+4$ become allowed through a mixing of rotational

$^\ddagger \text{CH}_3\text{CH}$: ref. [4]; CH_3I : ref. [5]; CHCl_3 : ref. [6].

wavefunctions, a direct consequence of the rotation—translation coupling perturbation. This significant perturbation arises because of the asymmetric mass distribution of HD. This effect, so pronounced in this most simple of systems, must also be present in other fluids [8] but is concealed and not easily distinguished when individual fine structure is not resolved. The optically active systems considered in this letter provide another subtle way for observing these effects (see also the work of Baranova and Zel'dovich [9]).

This poses significant problems for the molecular dynamicist. The natural development of the field [3], since the pioneering days of Debye, has been through the elaboration of molecular models based on the rotational motions of molecules and the effects of rotation—translation interaction have been neglected. Theories for the latter are either intractable or contain numerous adjustable parameters, its development still being in its infancy. The neglect of this coupling interaction may be part of the reason for the slight confusion that exists between results obtained from different experimental techniques [2,3]. However, there are still significant uncertainties associated with the experimental techniques themselves and with the subsequent reduction of the data to a form suitable for comparison with theory [3].

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References

- [1] M.W. Evans, *Phys. Rev. Letters*, to be published.
- [2] L.A. Nafie, P.L. Polavarapu and M. Diem, *J. Chem. Phys.* 73 (1980) 3530.
- [3] M.W. Evans, G.J. Evans, W.T. Coffey and P. Grigolini, *Molecular dynamics* (Wiley—Interscience, New York, 1982).
- [4] M.W. Evans, *Advan. Mol. Relax. Interaction Processes*, to be published.
- [5] G.J. Evans and M.W. Evans, *Advan. Mol. Relax. Interaction Processes*, to be published.
- [6] G.J. Evans and M.W. Evans, *Advan. Mol. Relax. Interaction Processes*, to be published.
- [7] G. Ewing, *Accounts Chem. Res.* 2 (1968) 168.
- [8] H.L. Welsh, *MTP International Review of Science, Phys. Chem. Series 1, 3*, ed. D.A. Ramsay (Butterworths, London, 1972).
- [9] N.B. Baranova and B.Ya. Zel'dovich, *Chem. Phys. Letters* 57 (1978) 435.