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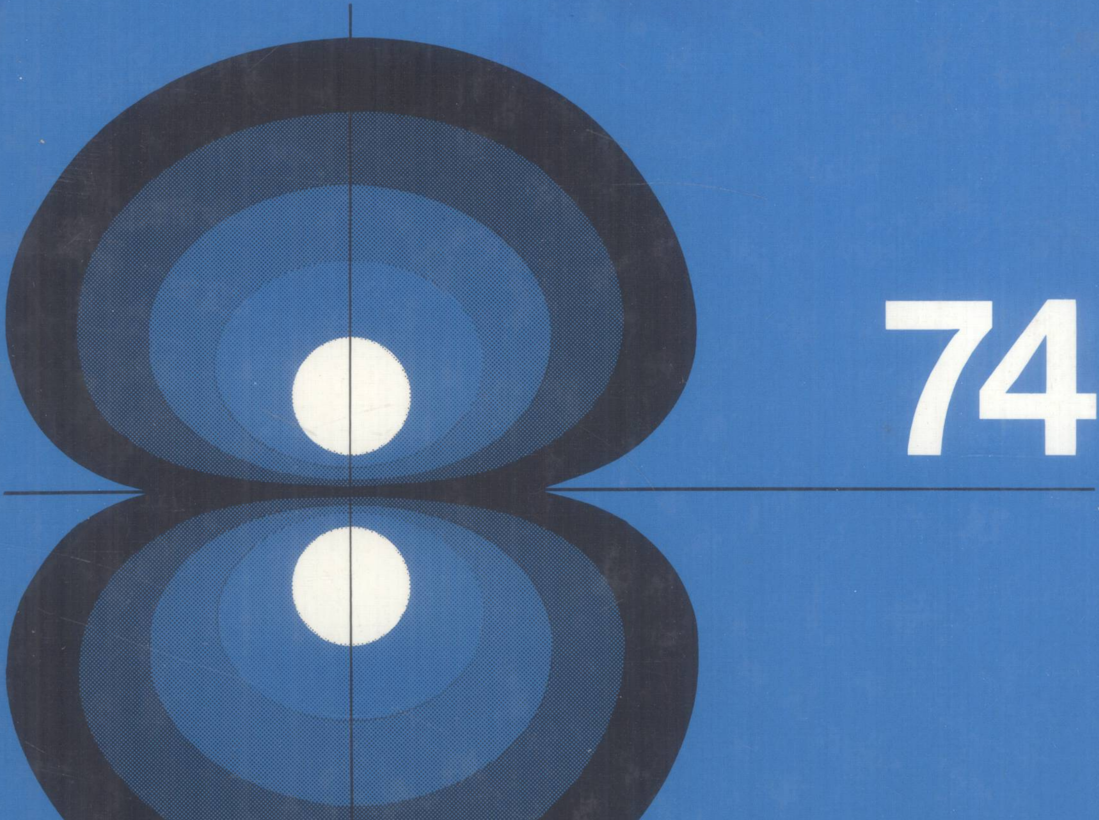

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SPECTROSCOPY AND RELAXATION OF MOLECULAR LIQUIDS

Edited by
D. Steele
and
J. Yarwood

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SPECTROSCOPY AND RELAXATION OF MOLECULAR LIQUIDS

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PREFACE

When we started to plan this book (it seems a long time ago!) we intended to produce an edited text comprising chapters by experts in the different areas involved with the determination of intermolecular forces and dynamics in (relatively simple) liquids. It was not intended as an up-to-date review; rather we aimed to produce a graduate text book aimed at new research students or more mature scientists new to the field. Each chapter contains the theoretical foundation relevant to that particular technique, while chapter 2 presents fundamental concepts, definitions and mathematical operations common to all work on the statistical mechanics of the liquid phase. We asked each author to provide some examples of how their technique had been applied to particular systems. In this way we hoped to illustrate the usefulness of each experimental or theoretical approach. All our colleagues have avoided the prescriptive approach; for good reasons - such an approach does not work! Every individual molecular liquid has to be treated on its own merits and "handle turning" is simply not "on". This is what gives the area of liquid phase dynamics its richness and diversity. It also presents considerable and very persistent difficulties, both theoretical and experimental. We simply do not understand fully enough the (dynamic) intermolecular potentials in even simple fluids. The authors have not tried to avoid the difficulties. Few molecular liquids could be said to have had their dynamic behaviour fully elucidated. Such is the challenge of the approaching 21st century in this, the "last frontier" of molecular physics and chemistry.

One is therefore tempted to ask, whether the effort is worthwhile. We believe it is; if only because the chemical reactivity of molecular encounters in fluids (and most reactions are carried out in the liquid phase) is controlled by their relative dynamic and interactive properties. So, if we are ever to predict and control the course of a particular reaction (let alone design new reactions), we need to understand how molecules move and interact. But the potential benefits of a real understanding are much wider in some senses. Industry uses (indeed, relies upon) and sells a wide range of fluid materials (from liquid nitrogen to complicated colloidal dispersions) with which we enrich our daily lives. Very little fundamental understanding of molecular behaviour (at microscopic level) goes into the formulation of a shampoo or engine oil, but until we do have such understanding such important and useful commodities will be produced by strategies which are at best empirical, and at worst alchemical! Some considerable progress has been made in the last five years towards the elucidation of the structure and dynamics of more complex fluids (Chapter 1). This book largely concentrates on the simpler fluids; the philosophy being that fundamental work on simple liquids might give us the "tools" needed in order to tackle more complicated systems.

We are grateful to our authors for their efforts and, in some cases for their patience, during the preparation of this book. Without their hard work no text of this nature would have been possible. We also owe sincere thanks to those who helped in the preparation, especially Mrs A Carrahar and Mrs E Wood at Durham and Mrs J Evans at RHBNC.

D. Steele, London

J. Yarwood, Durham October 1990

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Glossary of Symbols

A_ν	Absorbance $\log_e (I_o/I)_\nu$
Å	An Angstrom unit (10^{-8}cm ≡ 10^{-10}m)
$\underset{\sim}{\alpha}$	polarisability tensor
$\bar{\alpha}$	mean polarisability
α_i	principal polarisability components
$\alpha(\nu)$	the absorption coefficient at frequency ν
$\hat{a}_{ij}(\nu)$	the complex propagation factor
B_{if}	transition probability
$\underset{\sim}{\beta}$	hyperpolarisability
β	$1/k_BT$; Fuoss Kirkwood distribution factor
c	concentration (normal)
c'	velocity of light in vacuum
C_v, C_p	specific heats
$C_\omega(t)$	the angular momentum correlation function
$C_{\ell R}(t)$	the molecular ℓ^{th} order correlation function for rotation
$C_v(t)$	the molecular vibrational correlation function
γ	polarisability anisotropy
Γ_ν	$\frac{1}{\nu} A_\nu$
d(or ℓ)	path length or medium thickness
D_{xx}	Rotational diffusion constant
D	Wigner rotation matrix
$\underset{\sim}{\hat{e}}_x$	unit vector along x
$\epsilon(\omega)$	Permittivity at frequency ω
ϵ_o	Permittivity of vacuum (free space)
$\hat{\epsilon}(\nu)$	complex permittivity = $\epsilon'(\nu) + i\,\epsilon''(\nu)$
$\underset{\sim}{\hat{E}}$	Electric field vector (in general, complex)
$\dot{f}_\ell$	dynamic correlation factor
Φ_T	the total dipole density correlation function

g_ℓ	static ℓ^{th} order correlation factor
$G_T(\nu)$	the internal local field factor (in general)
h	Planck constant
H	Hamiltonian Operator
Θ	quadrupole moment
$\underset{\sim}{\boldsymbol{I}}$	Unit Matrix
I_{int}	Integrated intensity
I_σ	moment of inertia along the σ cartesian direction
I_o, I	Incident and transmitted radiant intensity
$\mathbf{J}$	angular momentum
$\underset{\sim}{\mathbf{k}}, \underset{\sim}{\mathbf{q}}$	wave vector, scattering vector
$k_{ij}(\nu)$	the absorption index - frequency dependence
k_B	Boltmann constant
$K_\ell(t)$	The ℓ^{th} order memory function
$\hat{L}(\nu)$	the complex insertion loss as a function of frequency
λ	wavelength
M_n M_{nv} M_{nR}	n^{th} order normalised intensity moments for vibrational and rotational band profiles
$\underset{\sim}{\mathbf{M}}_{\mathbf{i}}$	total dipole density (- as per P.A. Madden / Buckingham)
$\underset{\sim}{\mathbf{M}}_{\mathbf{I}}$	total (electric field) induced dipole density
$\underset{\sim}{\boldsymbol{\mu}}$	molecular dipole moment -(permanent dipole moment - individual molecule)
$\partial\mu/\partial Q$	transition dipole moment (usually measurements on bands intensities in liquids will give $\partial M/\partial Q$ - however, the notation $\partial\mu/\partial Q$ is universal in intensity theory and is preserved here)
M	Relative Molecular Mass
$\hat{n}(\tilde{\nu})$	complex refractive coefficient at frequency ν
N_o	Avogadro's Number
N_i	level populations
$\langle N^2 \rangle$	Intermolecular torque
ν	frequency

$\tilde{\nu}$ $(= \frac{1}{\lambda})$	wavenumber [$\omega = 2\Pi \tilde{\nu} c$]
ν_o	the true vibrational energy zero (0,0 rotational transition)
ν_ℓ	incident laser frequency
$\Delta\nu_{1/2}$	FWHM - the full half band width
$P_\ell(\mathrm{Cos}\ \theta)$	ℓ^{th} order Legendre polynomial in Cos θ
π_i	molecular polarisability
Π	total system polarisability
$Q_{\ell i}$	normal coordinate of ℓ^{th} mode of i^{th} molecule
$\underset{\sim}{q}$	wave vector of scattered light = $\underset{\sim}{k}_f - \underset{\sim}{k}_i$
ρ	molecular density
ρ	flux density
$R_{i(\nu)}$	the power reflection coefficient
$\hat{r}_{ij}$, $\hat{t}_{ij}$	reflection and transmission amplitudes
$\hat{S}(\nu)$	the complex spectrum as a function of frequency
T	absolute (Kelvin) temperature
T_ρ	Torque component
$T_{i(\nu)}$	the power transmission coefficient as a function of frequency
τ_v	the relaxation (correlation) time for vibrational dephasing
$d\tau$	volume element
$\tau_{\ell R}$	relaxation (correlation) time for rotation
t	time
u	unit vector along the direction of a dipole or transition dipole
$\underset{\sim}{U}$	transformation matrix
V_m	molar volume
$\underset{\sim}{v}'$	spatial derivative of vector **v**
$\underset{\sim}{\dot{v}}$	time derivative of vector **v**
$\underset{\sim}{v}(t)$	velocity vector (time dependent)
Ψ	molecular wave function
ω	angular frequency

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CHAPTER 1

INTRODUCTION

by Derek Steele and Jack Yarwood

The reader may reasonably ask why another book on liquid phase dynamics and interactions? There are many facets to the answer. The most important point is the difference between this book and other current books [1-4] on the liquid phase. They are all theoretically based. Neither students, nor more mature research workers new to the field, usually start with the theory. They start with either a piece of equipment or a computer programme and they start to worry about the theory only when they wish to interpret (i.e. understand) what they have measured (or simulated). The theory is ,of course,of *crucial* importance but we wanted (as a first priority) to provide a book which would be of immediate use to workers new to the area. We wanted to show how the concepts and techniques described are of value in the practical elucidation of liquid phase microscopic properties. We hope that this book will complement others in the area and provide a 'manual' for the experimental determination of relaxation functions and times. We have also attempted to show how information about the nature and extent of intermolecular forces in the liquid phase (the 'last frontier' of chemical physics) may be available and will help experimentalists and theoreticians to understand each other - an essential requirement for real progress in this area.

Secondly, we wanted to produce a book which covered the full range of spectroscopically-based techniques available. No other text covers the whole range. There is much to be learned from considerations of the region of time and space covered by the different techniques. Even simple considerations based on observation time ($^1/\omega_{obs}$) can be instructive. For example, it has long been appreciated that our perception of molecular complex formation [5,6] may be dramatically affected by the region of the spectrum examined. For historical reasons, the first spectroscopic observations to be made in this area were in the ultraviolet and visible regions[5,6] , where observation times i the 10^{-15} sec region are relevant ($\omega = 2\pi\nu = 2\pi\tilde{\nu}c'$ in rad sec^{-1}) From a simplistic viewpoint, if the lifetime of the observe state is less than that for one cycle ($1/\nu$) of the radiation then the state properties probed by the wave will not b observed. Infact the Heisenberg Uncertainty Principle shows u that we must replace ν in the above by ω. This principle may b stated

$$\Delta\omega.\Delta\tau \geqslant 1/2.$$

$\Delta\omega$ and $\Delta\tau$ are the uncertainties in radial frequency and lifetime. This indicates that the 'lifetime' of a species, or phenomenon, which can be detected is approximately $1/\omega$. Note that this is a lower limit and that the practical upper lifetimes observable depends on being able to see changes in the uncertainty in frequency- that is, a broadening of the spectral profile (e.g. see below for time scales observable by n.m.r.). For a 'complex' (or 'site' - see below) with a lifetime of say 10^{-12} seconds such ultraviolet observations would lead to the conclusion that the complex was "long-lived", as indeed it is on the time scale of the observation. Incidentally (but sometimes not obviously) the same comment applies to X-ray or neutron diffraction measurements [7,8] where $1/\omega_{obs}$ is even shorter. On the other hand, observation in the far-infrared ($1/\omega_{obs} \cong 10^{-12}$ sec.) or microwave ($1/\omega_{obs} \cong 10^{-10}$ sec.) may lead to data whose interpretation require the consideration of 'site' interchange or complex dissociation o the time scale of the experiment[9,10]. Such considerations e apply to the mid-infrared regions ($1/\omega_{obs} \cong 10^{-14}$ sec.) exchange is fast (or lifetimes very low). For n.m.r. measureme where, although $1/\omega_{obs} = 1/(2\pi\nu) \simeq 10^{-6}$ to 10^{-8} seconds, the narrowness of the lines gives rise to an extended 'nmr time scale' which typically spans 1 second to 10^{-6} seconds. The 'complex' properties are thus said to be averaged over the relatively long observation time of the magnetic resonance technique. Of course, exchange of molecules between sites (equation 1.1)

$$A^{(1)} + B \underset{k_{21}}{\overset{k_{12}}{\leftrightarrows}} A^{(2)}B \qquad (1.1)$$