AN EXTENDED FRACTION REPRESENTATION OF THE CORRELATION FUNCTION
OF INDUCED ABSORPTION IN LIQUID MIXTURES

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A truncated Mori expansion of the correlation function is used to reproduce far infrared absorption data for mixtures of (i) benzene and carbon tetrachloride, (ii) iodine and benzene, (iii) iodine and carbon disulphide, (iv) bromine and carbon disulphide at ambient temperature. The experimental bands are matched adequately well over the frequency range $10-200$ cm^{-1}, but the data available are too limited in accuracy and temperature/pressure range to enable any firm conclusions to be made about effects such as "charge-transfer" complexing.

1. Introduction

In three recent papers [1] a preliminary investigation was made into the behaviour of the correlation function [2] $(c(t))$ associated with the far infrared [3] induced absorption in liquids consisting of non-dipolar molecules. It was discovered that $c(t)$ could be simulated closely by a truncated Mori expansion [4]. This series approximation is an attempt to keep the classical correlation function reversible in time $(c(t) = c(-t))$, i.e. to satisfy the Onsager reversibility principle, by assuming that every process which is statistically non-markovian [2] can be considered as the result of a "higher-order" markovian one. The correlation function can be represented in terms of a memory function [4] $(K(t))$, which has simpler analytical dependence on t than $c(t)$ itself. The connecting equation is an integro-differential type (Volterra equation) which is solved by Laplace transformation. Kubo has shown [5] in his second fluctuation-dissipation theorem that K is itself a correlation func-

tion, and Mori's theorem [4] asserts that the mathematical set of memory functions is such that the latter are interrelated by coupled Volterra equations involving the higher order memory functions $K_1, ..., K_N$. Thus K_1 is the memory function of K_0 etc.

Eventually, one of the functions K_N is assumed to be the correlation function of a stochastic process F_N (generally the Nth order derivative with respect to time of a linear or angular force) which is statistically markovian. This means that the conditional probability distribution [2] for the set of F_N at any future instant, given the present state, is unaffected by any additional knowledge of the past history of the system. For example if K were the correlation function of the set of markovian random torques F, i.e.

$$\langle \Omega(0) \cdot \Omega(0) \rangle K = \langle F(0) \cdot F(t) \rangle = K_0(0) \exp(-\beta t), \quad (1)$$

with Ω as the angular momentum, then changes in Ω would be instantaneous, molecular impacts would be perfectly elastic. The second equality in eq. (1) results from Doob's theorem [6], which states that the autocorrelation function of a Markov random variable [2] is exponential.

Naturally, there are some difficulties in the use of

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a Mori representation, e.g. if a memory function at some stage N is deemed to be exponential, then the violation of Onsager's principle is transferred merely from $c(t)$ to $K_N(t)$. Also, there arise equilibrium averages $K_0(0), \ldots, K_N(0)$ which are not known analytically because they are dependent upon the detailed dynamical behaviour of local interacting molecules in a dense fluid. Thus we cannot avoid the ultimate necessity of modelling, when using Mori–Kubo formalism. However, this representation seems to be satisfactory [1,4] on the very general statistical level, from which we do not stray in this brief paper, which is concerned with binary (A/B) mixtures of non-dipolar molecules in the dense liquid state. Here $c(t)$ is made up of contributions of type AA, AB and BB molecular interactions. Explicitly, the systems treated are carbon tetrachloride/benzene, I_2/benzene, Br_2/CS_2, and I_2/CS_2 at various concentrations. Solutions of iodine in non-dipolar solvents have been described as forming "charge-transfer" AB type complexes arising from molecular interactions upon collision, and have been studied in the far infrared by Kettle and Price [8]. In simulating their results with the Mori formalism, we will look for behaviour extraordinary compared with that of our "standard", the CCl_4/benzene solution, i.e. for an indication of complexing. The CCl_4/benzene solutions would seem to be ideal as "standard" solutions, however, there is some evidence [9] that crystalline mixtures of the two components do exhibit some complex formation. Conversely, this work and earlier submillimetre-wave studies [7,10] show *no indication* of complexing in solution.

2. Results and discussion

 . In computing the theoretical curves in figs. 1a to 1c we have made three hypotheses which we do not attempt to justify here except on the grounds that the experimental data are reproduced well enough if we make them. They are as follows.

(i) The correlation function of a mixture of non-dipolar molecules A and B can be expressed in the form:

$$C_{AB}(t) = \sum_{ij} [\langle {}^A\boldsymbol{\mu}_i(0) \cdot {}^A\boldsymbol{\mu}_j(t)\rangle + \langle {}^B\boldsymbol{\mu}_i(0) \cdot {}^B\boldsymbol{\mu}_j(t)\rangle$$
$$+ \langle {}^A\boldsymbol{\mu}_i(0) \cdot {}^B\boldsymbol{\mu}_j(t)\rangle + \langle {}^B\boldsymbol{\mu}_i(0) \cdot {}^A\boldsymbol{\mu}_j(t)\rangle] / C_{AB}(0), (2)$$
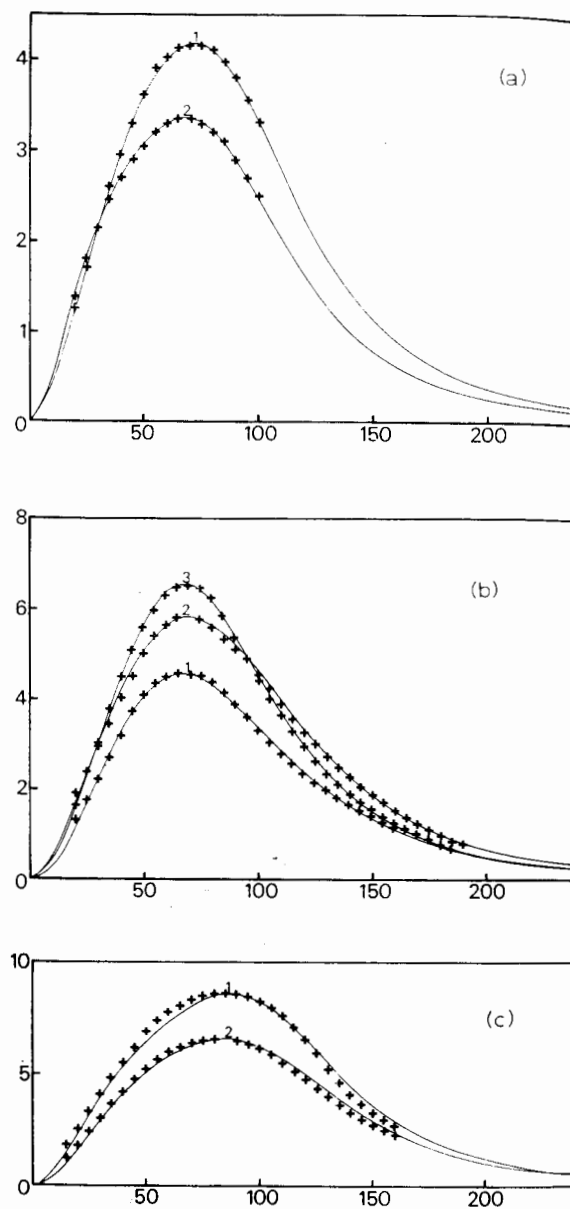

Fig. 1. (a) Solutions of carbon tetrachloride in benzene at 296 K. + Experimental [7]. (1) 2.588 mol dm^{-3} CCl$_4$; (2) 5.176 mol dm^{-3}. — Truncated Mori expansion, least mean squares best fit. (b) Solutions of Br$_2$ and I$_2$ in CS$_2$ at 294 K. + Experimental [8]. (1) 0.21 mol dm^{-3} of I$_2$; (3) 0.60 mol dm^{-3} of I$_2$; (2) 0.60 mol dm^{-3} of Br$_2$. — Truncated Mori expansion, least mean squares best fit. (c) Solution of I$_2$ in benzene at 296 K. + Experimental [8]. (1) 0.69 mol dm^{-3} of I$_2$; (2) 0.30 mol dm^{-3} of I$_2$. — Truncated Mori expansion, least mean squares best fit. Ordinate: $\alpha(\bar{\nu})$/neper cm^{-1}; abscissa: $\bar{\nu}$/cm^{-1}.

where $^A\mu_i(0)$, for example, is the magnitude and direction of the induced dipole moment (whatever the mechanism of induction may be [7]) of a molecule i of type A at the instant $t = 0$. The sum is over all pairs (i, j) such that none is counted more than once. The function is normalised to unity at $t = 0$ by dividing with $C_{AB}(0)$. So $C_{AB}(t)$ is the Fourier transform of the normalised spectral density [2] of the far infrared bands in which we are interested.

(ii) $C_{AB}(t)$ can be written within the integro-differential relation [5]:

$$\dot{C}_{AB}(t) = -\int_0^t K_{AB}(t-\tau) C_{AB}(\tau) \, d\tau , \qquad (3)$$

with the memory function K_{AB} having its own set of associated memory functions [4] $(^{(N)}K_{AB}(t), N \to \infty)$ related to it by a set of equations such as (3). We truncate [1,4] this series so that the random process of which $^{(1)}K_{AB}(t)$ is the correlation function is markovian [2], i.e.

$$^{(1)}K_{AB}(t) = {}^{(1)}K_{AB}(0) \exp(-\gamma t) . \qquad (4)$$

(iii) The bands arise from classical motions so that:

$$\alpha(\omega) = \frac{\omega^2 (\epsilon_0 - \epsilon_\infty)}{n(\omega)c} \, \text{Re} \, [C_{AB}(i\omega)] , \qquad (5)$$

where $\alpha(\omega)$ is the absorption coefficient [3] per unit path length of absorber (neper cm^{-1}), ω the frequency (rad s^{-1}), $n(\omega)$ the refractive index (constant within $\pm 2\%$ [7] for these weak absorbers), $(\epsilon_0 - \epsilon_\infty)$ the total dispersion and $C_{AB}(i\omega)$ the Fourier/Laplace transform of $C_{AB}(t)$.

More precisely, in eq. (5) ω^2 ought to be replaced by:

$$(2kT\omega/\hbar) \tanh(\hbar\omega/2kT) ,$$

but in practice, it has been found that this makes very little difference, except at the highest frequencies.

Our equation [1] for $\alpha(\omega)$ then contains the equilibrium average $^{(0)}K_{AB}(0)$ and $^{(1)}K_{AB}(0)$, with the units of s^{-2}, and γ^{-1}, a correlation time. These are adjusted to obtain the least mean squares best fit with the experimental data, and are given in table 1 for the mixtures studied here. All results are at $296 \pm 2K$. These quantities are probably complicated functions of the ensemble hamiltonian at equilibrium, and our data are too limited to allow us to arrive at anything except a tentative conclusion, but it is fairly clear from the table that the triad $^{(0)}K_{AB}(0)$, $^{(1)}K_{AB}(0)$ and γ go through a maximum at low concentrations of iodine in both benzene and CS_2, whereas the trend in CCl_4/benzene is almost entirely one of monotonic change from the benzene triad to that of CCl_4.

We conclude therefore that as a simple quantitative method of reproducing and comparing far infrared bandshapes of induced absorption in liquids and liquid mixtures the above is satisfactory, but in searching for signs of subtle effects such as "complexing" we will need more, and more accurate, data, over a far wider range of frequency, temperature, and molecular number density.

Table 1
Empirical factors in the truncated Mori spectrum

Solution	Concentration (mol dm^{-3})	$10^{-24}\, {}^{(0)}K_{AB}(0)$ (s^{-2})	$10^{-24}\, {}^{(1)}K_{AB}(0)$ (s^{-2})	$10^{-12}\, \gamma$ (s^{-1})
CCl$_4$/benzene	7.764	85	455	30
CCl$_4$/benzene	5.176	64	405	27
CCl$_4$	–	37	272	26
benzene	–	86	415	26
I$_2$/benzene	0.69	100	541	29
I$_2$/benzene	0.30	109	603	34
I$_2$/CS$_2$	0.60	92	448	34
I$_2$/CS$_2$	0.21	95	572	40
Br$_2$/CS$_2$	0.60	91	547	36
CS$_2$	–	83	540	36

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