MOMENT ANALYSIS OF THE MORI CONTINUED FRACTION: DIPOLAR ABSORPTION IN BROMOETHANE AND 1-BROMONAPHTHALENE

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The description of microwave and far infrared spectra with continued fractions is pursued using a moment analysis based on numerical integrals of the kind $\int_0^\infty \alpha(\bar{v}) \bar{v}^{2n} \, d\bar{v}$, where α is the power absorption coefficient (in neper cm^{-1}) and $\bar{v}$ the wavenumber in cm^{-1}. The theory is evaluated for bromoethane and 1-bromonaphthalene (pure liquids) at room temperature. The three and four variable truncations used are more successful for bromoethane than for 1-bromonaphthalene, where the sharp peak produced theoretically may be broadened and shifted only relaxing the conditions of v_{max}, the critical wavelength of the microwave data. Sum rules are developed for the moment integrals $\int_0^\infty \alpha(\bar{v}) \bar{v}^{2n} \, d\bar{v}$ and torque components evaluated.

1. Introduction and theory

The description of zero–THz spectra in molecular liquids is a formidable problem of statistical mechanics. The theory is only just beginning to reveal the intricacies behind the bland looking broad band spectra usually observable [1]. The only classical theoretical method available at present to match these features over a broad enough range of frequencies is the semi-empirical one based on expansions of the Liouville equation governing the N molecules of the system as a whole [2]. The Mori continued fraction is one such expansion, in terms of equilibrium ensemble averages, $K_0(0), \ldots, K_n(0)$ $(n \to \infty)$ of the relevant dynamical variables [3]. If we choose the orientational unit vector, u, these averages

are constructed as:

$$K_0(0) = \langle \dot{u}^2 \rangle, \tag{1}$$

$$K_1(0) = \langle \ddot{u}^2 \rangle / \langle \dot{u}^2 \rangle - \langle \dot{u}^2 \rangle. \tag{2}$$

If we define:

$$a_1 = -\langle \dot{u}^2 \rangle; \quad a_2 = \langle \ddot{u}^2 \rangle; \quad a_3 = -\langle \dddot{u}^2 \rangle,$$

then

$$K_2(0) = \langle 2a_1^4 - 2a_1^2 a_2 - a_1 a_3 + a_2^2 \rangle / a_1(a_2 - a_1^2). \tag{3}$$

This kind of analysis can be continued for higher $K_n(0)$ $(n \to \infty)$ (see appendix).

In principle, it is possible to obtain $K_n(0)$ for all n by a moment analysis of the appropriate spectral data. This is because

$$C(t) = \langle u(t) \cdot u(0) \rangle = \sum_{n=0}^\infty a_n \frac{t^{2n}}{(2n)!}. \tag{4}$$

If this is assumed then Evans et al. [4] have shown that when we ignore internal field corrections:

$$a_1 = -\Xi \int_0^\infty \alpha(\bar{v}) \, d\bar{v}, \tag{5}$$

$$a_2 = 4\pi^2 c^2 \Xi \int_0^\infty \bar{v}^2 \alpha(\bar{v}) \, d\bar{v}, \tag{6}$$

$$a_3 = -16\pi^4 c^4 \Xi \int_0^\infty \bar{v}^4 \alpha(\bar{v}) \, d\bar{v}, \tag{7}$$

with

$$\Xi = 3kTc^2/\pi N_1 \mu^2. \tag{8}$$

In eqs. (5)–(8), $\alpha(\bar{v})$ is the far infrared power absorption coefficient, in neper cm^{-1}, $\bar{v}$ the wavenumber (in cm^{-1}), N_1 the molecular number density, μ the molecular dipole moment and c the velocity of light. Eq. (5) is often known as the Gordon sum rule. These relations are obtained on the basis of the expansion:

$$C(t) = 1 - \langle \dot{u}^2 \rangle \frac{t^2}{2!} + \langle \ddot{u}^2 \rangle \frac{t^4}{4!} - \langle \dddot{u}^2 \rangle \frac{t^6}{6!} + \cdots, \tag{9}$$

which holds true in the absence of quantum effects. The quantum mechanical equivalent [1] of $C(t)$ may be expanded in a time series, *but the odd t terms no longer necessarily vanish*. It is frequently overlooked that the series expansion represented by eq. (9) *does not produce an acceptable spectrum* by Fourier transformation. Taken term by term we have, in Laplace space:

$$\tilde{C}(p) = \frac{1}{p} - \frac{\langle \dot{u}^2 \rangle}{p^3} + \frac{\langle \ddot{u}^2 \rangle}{p^5} - \frac{\langle \dddot{u}^2 \rangle}{p^7} + \cdots. \tag{10}$$

The real and imaginary parts of $\bar{C}(p)$ in the space of frequency (ω) are obtained using the substitution $p = -i\omega$. It is easily seen from eq. (10) that $\bar{C}(-i\omega)$ has no real part, and therefore is not a valid description of a relaxation spectrum, i.e. of loss and dispersion. *The rigorous quantum mechanical equivalent of $\bar{C}(-i\omega)$ on the other hand has a real and imaginary part.*

Mori [3] has expanded $\bar{C}(p)$ in a continued fraction:

$$\bar{C}(p) = \cfrac{1}{p + \cfrac{K_0(0)}{p + \cfrac{K_1(0)}{p + \ddots}}} \tag{11}$$

which is equivalent to eq. (10) if we take the continued fraction to infinity. Therefore eq. (11) also is not a valid description of a broad band relaxation spectrum *when untruncated*. This was first pointed out by Scaife [5] in 1976 in the context of autocorrelations of u. The rigorous quantum mechanical version of eq. (11) is of course equivalent to the quantum-mechanical version of eq. (10) and produces a well-defined spectrum. The more general Mori theory [6], derived for cross-correlation functions in addition to the autocorrelations of eqs. (10) and (11), uses column vectors of more than one dynamical variable, e.g. $\begin{bmatrix} u \\ \dot{u} \end{bmatrix}$. In general the Mori resonance operator does not vanish when taking into account cross-correlations.

Whenever eq. (11) has been used as a description of zero–THz spectra it has been closed with an ad-hoc assumption on the time dependence of $K_n(t)$, an nth memory function. A great deal of spectral comparison has been completed to date with the closure:

$$K_1(t) = K_1(0) \exp(-\gamma_1 t). \tag{12}$$

The analysis of this equation has not been entirely satisfactory because $K_1(0)$ and γ_1 have been treated as adjustable variables. In this paper we aim to resolve the question consistently without the use of fitting procedures, but rather through the acquisition or use of accurate spectra *over the complete zero–THz range*, especially in the high frequency wing area of the far infrared. Eqs. (1) to (7) can then be utilised to define the averages $K_n(0)$ unambiguously from the far infrared power absorption coefficient.

The frequency γ_1 is defined from the peak frequency (ω_1) of the dielectric loss ϵ'' through the equation

$$[d\epsilon''/d\omega]_{\omega_1} = 0. \tag{13}$$

(11)–(13) provide the relations:

$$\frac{-[K_0(0)+K_1(0)]\}\{5\omega_1^4 - \omega_1^2[K_0(0)+K_1(0)]\}}{[K_0(0)-\omega_1^2][K_0(0)+3\omega_1^2]}, \tag{14}$$

$$= (\epsilon_0 - n_\infty^2)\omega\gamma_1 K_0(0)K_1(0)/D, \tag{15}$$

$$= \epsilon_0 + (\epsilon_0 - n_\infty^2)\omega^2\{\gamma_1^2[K_0(0)-\omega^2]$$
$$\cdots\omega^2 - [K_0(0)+K_1(0)]][K_1(0)-\omega^2]\}/D, \tag{15}$$

$$= \omega^3 - \omega[K_0(0)+K_1(0)]\}^2 + \gamma_1^2[K_0(0)-\omega^2]\}^2, \tag{16}$$

ϵ_0 is the static permittivity, n_∞ the refractive index at the high frequency extremum of the zero–THz curve, ϵ'' the dielectric loss and ϵ' the frequency dependent permittivity. The far infrared power absorption coefficient is defined through the Maxwell relation:

$$= \omega\epsilon''(\omega)/n(\omega)c, \tag{17}$$

where

$$= \{\tfrac{1}{2}[(\epsilon'^2 + \epsilon''^2)^{1/2} + \epsilon']\}^{1/2},$$

the refractive index. With the usual relation $\omega = 2\pi \bar{v}c$ it is therefore possible to construct theoretically the moment spectra $\bar{v}^{2n}\alpha(\bar{v})$. The nature of the truncation, eq. (12) implies that $\bar{v}^4\alpha(\bar{v})$ will become a plateau theoretically as $\bar{v}\to\infty$. The $\bar{v}^4\alpha(\bar{v})$ spectrum, which is measured experimentally, albeit with some difficulty can be reproduced qualitatively only with the further assumption:

$$= K_2(0) \exp(-\gamma_2 t). \tag{18}$$

This equation implies that:

$$= (\epsilon_0 - n_\infty^2)\omega\gamma_2 K_0(0) K_1(0) K_2(0)/D_1, \tag{19}$$

$$= \epsilon_0 - (\epsilon_0 - n_\infty^2)\omega\{(\omega^3 - \omega[K_1(0)+K_2(0)])$$
$$\cdots^4 - \omega^2[K_0(0)+K_1(0)+K_2(0)] + K_0(0)K_2(0))$$
$$- \gamma_2^2\omega(\omega^2 - [K_0(0)+K_1(0)])$$
$$\cdots K_1(0) - \omega^2]\}/D_1; \tag{20}$$

$$= \omega^4 - \omega^2[K_0(0)+K_1(0)+K_2(0)]$$
$$\cdots K_0(0)K_2(0)\}^2 + \gamma_2^2\{\omega^3 - \omega[K_0(0)+K_1(0)]\}^2, \tag{21}$$

$$\gamma_2^2 = \{2\omega_1(4\omega_1^3 - 2\omega_1[K_0(0)+K_1(0)+K_2(0)])$$
$$\times (\omega_1^4 - \omega_1^2[K_0(0)+K_1(0)+K_2(0)]$$
$$+ K_0(0)K_2(0)) - (\omega_1^4 - \omega_1^2[K_0(0)+K_1(0)+K_2(0)]$$
$$+ K_0(0)K_2(0))^2\}\{\omega_1^2(\omega_1^2 - [K_0(0)+K_1(0)])$$
$$\times (-2(3\omega_1^2 - [K_0(0)+K_1(0)])$$
$$+ \omega_1^2 - [K_0(0)+K_1(0)])\}^{-1}. \tag{22}$$

Eqs. (3), (7) and (19)–(22) allow us to build up $\bar{v}^4\alpha(\bar{v})$ fairly satisfactorily but $\bar{v}^6\alpha(\bar{v})$ still develops a plateau theoretically as $\bar{v}\to\infty$. Obviously it is not useful to attempt to take the analysis further without adequate consideration of what is being generated by truncations further down the continued fraction.

2. Quantum effects and the continued fraction

The correlation function in quantum mechanics is based on the Heisenberg equation and has been discussed in detail by Gordon [7]. The truncation of the continued fraction according to eq. (12) or (18) introduces odd terms in the classical expansion (10), but still moment spectra such as $\bar{v}^6\alpha(\bar{v})$ are left undefined theoretically. On the other hand, if we take the continued fraction to infinity (always assuming that the classical autocorrelation function is infinitely differentiable) the spectrum is well defined because, as we have seen $\bar{C}(-i\omega)$ has no real part (or a vanishingly small real part). The continued fraction is derived by projection operations into subspaces of the complete Hilbert space spanned by the dynamical variables of interest and the starting point for this exercise is the classical Liouville equation of statistical mechanics. *There are paradoxes inherent therefore in the classical theory which may not be resolved by taking the continued fraction to infinity.* In the quantum-mechanical case the markovian assumption leads rigorously to the correct thermodynamical equilibrium. The breakdown of time-reversal invariance is an effect of the markovian assumption at the nth

order of Mori's hierarchy rather than of quantum origin. If we accept the classical projection procedures of Mori, Kubo, Zwanzig et al. [1] and the implied linearisation of the Euler equations governing molecular rotational motion then the classical theory must be replaced by the rigorous quantum theory in order to match without paradox observable spectral moments even when these are derived from *broad-band* spectra. This is a fundamental theorem which has not been foreseen to apply to relaxation spectra, in particular dielectric spectroscopy.

If we want to build up the autocorrelation function of the quantum mechanical operator $\hat{A}$, the classical commutative equation:

$$C(t) = \langle A(t)A(0)\rangle = \langle A(-t)A(0)\rangle = \langle A(0)A(-t)\rangle \tag{23}$$

no longer applies. The autocorrelation function, or scalar product, of $\hat{A}$ is no longer even in time, and has an imaginary part. The real part is even in time but the imaginary part is odd. The real and imaginary parts of the spectral density, $\rho\tilde{C}(\omega)$ and $\sigma C(\omega)$ respectively, are related by detailed balancing, so that:

$$\tilde{C}(-\omega) = \exp\left(-\hbar\omega/kT\right)\tilde{C}(\omega), \tag{24}$$

$$\sigma\tilde{C}(\omega) = \tanh\left(\hbar\omega/2kT\right)\rho\tilde{C}(\omega), \tag{25}$$

$$\tilde{C}(\omega) = [1 + \tanh\left(\hbar\omega/2kT\right)]\rho\tilde{C}(\omega). \tag{26}$$

Denoting by $\hat{R}$ and $\hat{I}$ the real and imaginary parts of the correlation function, it follows that

$$\rho\tilde{C}(\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} R\,C(t)\,\mathrm{e}^{i\omega t}\,\mathrm{d}t, \tag{27}$$

with

$$\hat{R}\tilde{C}(t) = \tfrac{1}{2}[C(t) + C(-t)]$$
$$= \tfrac{1}{2}[\langle\hat{A}(0)\hat{A}(t)\rangle + \langle\hat{A}(0)\hat{A}(-t)\rangle]. \tag{28}$$

Here $\hat{A}$ emphasises that A is to be regarded as a quantum mechanical *operator*. Eqs. (24)–(28) therefore imply that the further down the Mori continued fraction we truncate, i.e. the higher is γ_n (in THz), the more important will become the imaginary part of the quantum mechanical

correlation function. To reproduce the spectroscopically observable $\bar{v}^{2n}\alpha(\bar{v})$ we shall need the rigorously quantum mechanical Mori continued fraction. This is discussed in the literature (see r [1], chs. 9 and 10) in terms of the Redfield equa and its superoperators.

By spectroscopy and computer simulation it is seen that the real part of $C(t)$ behaves in a certain way, but these same spectra are capable of revealing also the imaginary part of $C(t)$, defined by

$$iIC(t) = \int_{-\infty}^{\infty} \sigma\tilde{C}(\omega)\,\mathrm{e}^{i\omega t}\,\mathrm{d}\omega. \tag{29}$$

As a first approximation the classical and quantum mechanical correlation functions are related by:

$$C(t) = C_{\mathrm{class}}(t - i\hbar/2kT). \tag{30}$$

In this paper we shall see how the purely classical Mori continued fraction works out with moment spectra [up to $\bar{v}^4\alpha(\bar{v})$] for liquid bromoethane, 2,2-dibromopropane and 1-bromonaphthalene, a series chosen partly for spectral convenience and partly because these three molecules typify in many respects the features observable in complete zero–THz frequency spectroscopy (i.e. dielectric, far infrared and higher moments).

3. Experimental

The spectra were obtained with three interferometers at Aberystwyth; Trinity College, Dublin; and Telecom, Martlesham Heath. A Grubb Parsons Mark III "cube" interferometer was used at Aberystwyth in the phase modulated mode of operation fully described elsewhere. These results were checked at TCD with an amplitude modulated interferometer of Grubb–Parsons/NPL mark I design. At Telecom a Martin–Puplett polarising interferometer was used with a liquid helium cooled Rollin detector to bridge the gap between the available MHz to GHz frequency data (of Smyth et al. [8]

example) and the far infrared.

The cell designs used were based on the RIIC
VC-01 variable path-length liquid cell incor-
porating quartz or poly (4 methyl pent-1-ene)
windows. Golay detectors were used to about
10 cm^{-1}, the low frequency limit of its range.

Various configurations were tried in an
attempt to optimise the high frequency wing of
the far infrared Poley absorption. The experi-
mental methods involved here are more fully
described elsewhere.

4. Results and discussion

The spectra are illustrated in figs. 1–3. The
lower frequency parts of these spectra (the
dielectric loss and dispersion) are available in
the literature, and have been used to fix γ_1 and
according to eqs. (14) and (22), respectively.

4.1. Bromoethane

The method used to match the experimental
data is firstly to attempt to reproduce as many
moments as possible using eq. (12), and then
to test for "convergence" using eq. (18), i.e.
ascertain how the theoretical spectra are
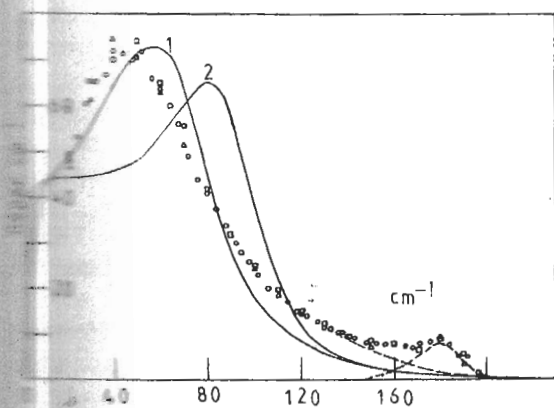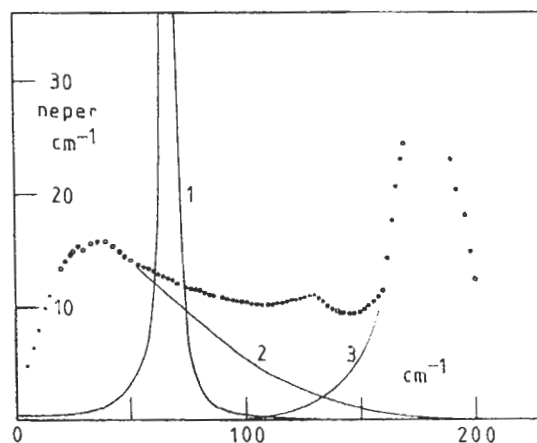affected by truncation further down the con-
tinued fraction.

Fig. 2. ⊙ Power absorption coefficient in neper cm^{-1}, of
liquid bromonaphthalene at 293 K. (1) Three- and four-
variable theory. (2) Extrapolated high frequency using of
liquid data. (3) Lorentzian extrapolation of a proper mode
to lower frequencies.

Bromoethane is a suitable simple liquid
because the far infrared spectrum (fig. 1) is free
of proper mode interference (see Durig et al.
[9]), and Hennelly et al. [8] have produced the
necessary lower frequency part of the total
zero–THz frequency profile. This is the so-
called zeroth spectral moment, the area under-
neath $\epsilon''(\omega)/\omega$. The classical Debye theory is
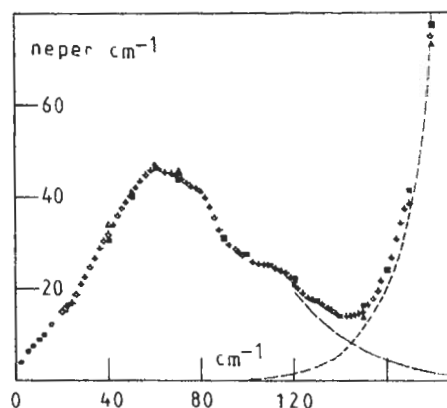capable of fitting this superficially, but produces

Fig. 1. Power absorption coefficient, in neper cm^{-1}, of
liquid bromoethane at 293 K. (1) Three-variable theory.
(2) Four-variable theory.

Fig. 3. Multi-decade profile of liquid 2,2-dibromopropane.
● Polarizing interferometers, 1–10 cm^{-1}. –⊙– Cube inter-
ferometers.

a plateau in the power absorption $\alpha(\bar{v})$, so that the area beneath $\alpha(\bar{v})$, i.e. the second spectral moment, is infinite for classical rotational diffusion.

Unfortunately, most of the available literature analysis of molecular diffusion in liquid bromoethane is still based on Debye's theory. For example Sempere and Regnier [10] have detected two spin–lattice relaxation times in the 213–373 K temperature range in liquid bromoethane and have compared these with Debye relaxation times. Adamenko and Chernyavs'ka [11] have investigated the translational and rotational diffusion of bromoethane using respectively viscous shear stress measurements and reorientational relaxation times from the anisotropic component of the Rayleigh light scattering. Plots of log(viscous shear stress) and log(reorientational relaxation time) versus I/T are linear in all cases. In an interesting paper Martin [12] obtained a glass of CH_3CH_2Br by differential thermal analysis. On heating, an endothermic process appears at a temperature T_v, where the glass softens and is transformed into a supercooled liquid by the appearance of free volume (holes), and at a temperature T_R the supercooled liquid recrystallises. X-ray powder spectra reveal no crystallisation below T_R. Infrared spectra prove that in the glassy and supercooled liquid states the same rotational isomers coexist that were observed in the liquid above T_F, the melting point. In the crystal only the trans isomer exists. NMR spectra show that between T_V and T_R a dynamic reorientation of the different segments of the hydrocarbon chain appears, which ceases in the crystal. Intense dielectric absorption between T_V and T_R confirms the reorientation of the polar group CH_2X, which produces a Cole/Davidson behaviour of ϵ'' when plotted against ϵ'. It would be interesting to monitor this thermal process with far infrared data, where the liquid state Poley absorption is transformed into the γ process of the viscous and glassy states, recently discovered and characterised by Reid and Evans [13]. The complete zero–THz spectrum in this case should of course include the far infrared γ feature.

The results of the Mori analysis are summarised for CH_3CH_2Br in fig. 1. From the moment analysis we have, using the proportionality constants of eq. (34), i.e. the observable liquid state $(\epsilon_0 - n_R^2)$, rather than the gas phase Ξ of eqs. (5)–(8) we have in the three-variable case: $\gamma_1 = 11.8$ THz; $K_0 = 4.1$ $(THz)^2$; $K_1 = 176.2$ $(THz)^2$; and in the four-variable case: $\gamma_2 = 22.2$ THz; $K_0 = 4.1$ $(THz)^2$; $K_1 = 176.2$ $(THz)^2$; and $K_2 = 254.4$ $(THz)^2$.

We have $\epsilon_0 = 9.22$; $n_\infty = 1.42$; and the dielectric loss peaks at 0.71 cm.

The intensity of the measured power absorption coefficient is matched very well, and the loss peak frequency is theoretically fixed at the value 0.71 cm. In the three variable case the moment analysis produces a fairly good positional fit and shape, but perhaps due to an overemphasis in the wings of $\bar{v}^4\alpha(\bar{v})$ the four-variable peak is shifted to higher frequencies, and consequently there is no sign of convergence in the continued fraction. It is probable that higher accuracy in the wings of the far infrared data will improve the overall fit.

4.2. 1-bromonaphthalene

This is a much more severe test for the three- or four-variable theory because the molecule is flat and an asymmetric diffuser with moments of inertia $I_A = 5.97 \times 10^{-38}$ gm cm^2; $I_B = 1.32 \times 10^{-37}$ gm cm^2; $I_C = 1.92 \times 10^{-37}$ gm cm^2. The dielectric permittivity at static frequency is $\epsilon_0 = 4.83$; with a D line refractive index of $n_D = 1.658$. The dielectric loss peak wavelength is $v = 16.2$ cm, well separated from the far infrared peak frequency at $\bar{v} = 38 \pm 3$ cm^{-1}.

These data provide us with the three-variable result: $\gamma_1 = 0.52$ THz; $K_0 = 3.6$ $(THz)^2$; $K_1 = 157.2$ $(THz)^2$; and in the four-variable case: $\gamma_2 = 451$ THz; $K_0 = 3.6$ $(THz)^2$; $K_1 = 157.2$ $(THz)^2$; $K_2 = 232.5$ $(THz)^2$. However, the theoretical loss sectrum is now far too sharp (fig. 2) in both cases. This is a phenomenon well-known from the work of Reid and Evans [1, ch. 4] on the Mori continued fraction applied to the angular velocity. The situation

be improved by allowing K_0, K_1 and γ to vary, i.e. allowing both the microwave and far infrared peak frequencies to vary theoretically.

As demonstrated by Reid and Evans this produces a much better fit to the far infrared spectrum, but with the microwave critical frequency about 50% too high. There is, of course, a further difficulty with applying projection method to asymmetric rotational diffusion because nonlinearities of the Euler/Langevin equations are projected into the random noise term, necessitating, among other things, the use of a reduced moment of inertia I_r, as defined by Reid and Evans [1, ch.4].

The situation in 2,2-dibromopropane is intermediate.

4.3. Analysis of spectra in terms of mean square torque sum rules

The areas under the $\alpha(\omega)$ versus ω and $\omega^2 \alpha(\omega)$ versus ω curve may be calculated in the manner of Gordon [7] and Bordewijk and Bottcher [14] who have given expressions for $\langle \dot{u}(0) \cdot \dot{u}(0) \rangle$ and $\langle \ddot{u}(0) \cdot \ddot{u}(0) \rangle$. These are, for the asymmetric top:

$$\langle \dot{u}(0) \cdot \dot{u}(0) \rangle = \langle \omega_1^2 \rangle (u_2^2 + u_3^2)$$
$$+ \langle \omega_2^2 \rangle (u_1^2 + u_3^2) + \langle \omega_3^2 \rangle (u_2^2 + u_3^2)$$
$$= kT \left(\frac{u_1^2 + u_2^2}{I_3} + \frac{u_1^2 + u_3^2}{I_2} + \frac{u_2^2 + u_3^2}{I_1} \right), \qquad (31)$$

where I_1, I_2 and I_3 are the principal moments of inertia and u_1, u_2 and u_3 components of the dipole unit vector u. Eq. (31) is of course the well known Gordon sum rule for $\int_0^\infty \alpha(\omega) \, d\omega$, apart from a constant factor given by Brot [15].

This kind of analysis can be extended using the kinematic relations (the Euler equations):

$$\ddot{u}_1 = \dot{\omega}_2 + \omega_1 \omega_3$$
$$= \frac{T_2}{I_2} + \omega_1 \omega_3 \left(\frac{-I_1 + I_2 + I_3}{I_2} \right),$$

$$\ddot{u}_2 = -\dot{\omega}_1 + \omega_2 \omega_3 = -\frac{T_1}{I_1} + \omega_2 \omega_3 \left(\frac{I_1 - I_2 + I_3}{I_1} \right),$$

$$\ddot{u}_3 = -\omega_1^2 - \omega_2^2.$$

Here T_1 and T_2 are components of the total torque T, defined by Bordewijk et al.

$$T = \dot{J} = \sum_i m_i r_i \times \ddot{r}_i.$$

Assuming that the components of ω and T are all independent, and averaging ω_i^2 and ω_i^4 we have:

$$\langle \ddot{u}(0) \cdot \ddot{u}(0) \rangle = \frac{\langle T_1^2 \rangle}{I_1^2} + \frac{\langle T_2^2 \rangle}{I_2^2}$$
$$+ \frac{(kT)^2}{I_1^2 I_2^2 I_3^2} \{ I_3[8 I_1 I_2 + I_3(I_1 + I_2)]$$
$$+ (I_1 - I_2)^2 (I_1 + I_2 + I_3) \}. \qquad (32)$$

Here eq. (32) is in effect the sum rule for

$$\int_0^\infty \omega^2 \alpha(\omega) \, d\omega,$$

apart from a constant term, taking into account, among other things, the effect of the internal field.

Similarly we may construct a sum rule for $\int_0^\infty \omega^4 \alpha(\omega) \, d\omega$ from the equilibrium average:

$$\langle \dddot{u}(0) \cdot \dddot{u}(0) \rangle,$$

given by:

$$\langle \dddot{u}(0) \cdot \dddot{u}(0) \rangle = \langle \dddot{u}_1^2(0) \rangle + \langle \dddot{u}_2^2(0) \rangle + \langle \dddot{u}_3^2(0) \rangle, \qquad (33)$$

with

$$\dddot{u}_1 = \frac{\dot{T}_2}{I_2} + \left(\frac{-I_1 + I_2 + I_3}{I_2} \right) (\dot{\omega}_1 \omega_3 + \omega_1 \dot{\omega}_3),$$

$$\dddot{u}_2 = -\frac{\dot{T}_1}{I_1} + \left(\frac{I_1 - I_2 + I_3}{I_1} \right) (\dot{\omega}_2 \omega_3 + \omega_2 \dot{\omega}_3),$$

$$\dddot{u}_3 = -2(\omega_1 \dot{\omega}_1 + \omega_2 \dot{\omega}_2),$$

$$\dot{\omega}_1 = [T_1 + \omega_2 \omega_3 (I_2 - I_3)]/I_1,$$

$$\dot{\omega}_2 = [T_2 + \omega_1 \omega_3 (I_3 - I_1)]/I_2,$$

$$\dot{\omega}_3 = [T_3 + \omega_1 \omega_2 (I_1 - I_2)]/I_3.$$

Consequently, at $t = 0$,

$$\langle \ddot{u}_i^2 \rangle = \frac{\langle \dot{T}_2^2 \rangle}{I_2^2} + \left(\frac{I_2 + I_3 - I_1}{I_2} \right)^2$$

$$\times \left[\frac{\langle \omega_3^2 \rangle \langle T_1^2 \rangle}{I_1^2} + \left(\frac{I_2 - I_3}{I_1} \right)^2 \langle \omega_2^2 \rangle \langle \omega_3^4 \rangle \right.$$

$$+ \frac{\langle \omega_1^2 \rangle \langle T_3^2 \rangle}{I_3^2} + \left(\frac{I_1 - I_2}{I_3} \right)^2 \langle \omega_1^4 \rangle \langle \omega_2^2 \rangle$$

$$\left. + \frac{2(I_2 - I_3)(I_1 - I_2)}{I_1 I_3} \langle \omega_1^2 \rangle \langle \omega_2^2 \rangle \langle \omega_3^2 \rangle \right],$$

where $i = 1, 2$, in permutation.

$$\langle \ddot{u}_3^2 \rangle = 4 \langle \omega_1^2 \dot{\omega}_1^2 \rangle + 8 \langle \omega_1 \dot{\omega}_1 \omega_2 \dot{\omega}_2 \rangle + 4 \langle \omega_2^2 \dot{\omega}_2^2 \rangle.$$

With Boltzmann statistics we have:

$$\langle \omega_i^{2n} \rangle = \left[\int_{-\infty}^{\infty} d\omega_i \, \omega_i^{2n} \exp \left(-\tfrac{1}{2} I_i \omega_i^2 / kT \right) \right]$$

$$\times \left[\int_{-\infty}^{\infty} d\omega_i \exp \left(-\tfrac{1}{2} I_i \omega_i^2 / kT \right) \right]^{-1}$$

$$= [(2n)!/n!](kT/2I_i)^n.$$

The sum rule for $\int_0^\infty \omega^4 \alpha(\omega) \, d\omega$ therefore involves both the mean square torque and the mean square torque derivative. Finally the general constant of proportionality is given by:

$$\langle u^{(n)} \cdot u^{(n)} \rangle = \frac{2}{\pi(\epsilon_0 - \epsilon_\infty)} \int_0^\infty \epsilon''(\omega) \omega^{2n-1} \, d\omega,$$

$$\alpha(\omega) = \omega \epsilon''(\omega)/n(\omega)c,$$

so that

$$\langle u^{(n)} \cdot u^{(n)} \rangle = \frac{2nc(2\pi c)^{2n-1}}{\pi(\epsilon_0 - \epsilon_\infty)} \int_0^\infty \alpha(\bar{v}) \bar{v}^{2n-2} \, d\bar{v}, \quad (34)$$

taking $n(\omega)$ as approximately constant.

Acknowledgement

Appendix

$C(t)$ satisfies the integro-differential equation

$$\frac{dC(t)}{dt} = -\int_0^t K_0(t - \tau) C(\tau) \, d\tau, \quad (A.1$$

where the memory function K_0 is defined by a similar integro-differential equation:

$$\frac{dK_0(t)}{dt} = -\int_0^t K_1(t - \tau) K_0(\tau) \, d\tau, \quad (A.2$$

and so on for K_m.

If we assume that

$$C(t) = \sum_n a_n t^n / n!, \quad (A.3$$

$$K_0(t) = \sum_n k_{0n} t^n / n!, \quad (A.4$$

$$\vdots$$

$$K_m(t) = \sum_m k_{mn} t^n / n!, \quad (A.5$$

then it is possible to express $K_0(0), \ldots, K_m(0)$ i terms of the coefficients a_n of eq. (A.3). For example:

$$\frac{a_1}{p^2} + \frac{a_2}{p^4} + \cdots = -\left(\frac{1}{p} + \frac{a_1}{p^3} + \cdots \right)$$

$$\times \left(\frac{k_{00}}{p} + \frac{k_{01}}{p^2} + \cdots \right),$$

so that comparing coefficients gives:

$$k_{00} = -a_1; \quad k_{01} = a_1^2 - a_2; \quad k_{02} = a_1^3 - a_3. \quad (A.6$$

Similarly:

$$k_{11} = -k_{20} k_{10},$$

$$k_{02} = -(k_{10} k_{01} + k_{11} k_{00}), \quad (A.7$$

so that

$$K_1(0) = k_{10} = a_1 - a_2/a_1, \quad (A.8$$

$$k_{20} = [a_1^4 - a_1 a_3 + (a_1^2 - a_2)^2]/a_1(a_2 - a_1^2). \tag{A.9}$$

This process can be continued but becomes tedious algebraically.

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