Mean square torques from far infrared spectra

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The moment analysis of far infrared spectra is used to estimate mean square torques for some dipolar solutes in decalin solution. These are compared with some model dependent values of Reid and Evans.

INTRODUCTION

In this paper we discuss the role of spectral moments in estimating mean square torques from far infrared and dielectric spectroscopy. The method developed here effectively extends the Gordon sum rule first used by Davies *et al.*[1] with the far infrared second moment. The method is model independent, and allows us an independent check on the mean square torques first developed by Reid and Evans[2] in their volume of rotation analysis reported previously.

From this analysis the molecular mean square torque (T_q) was extended on the basis of a model of the molecular liquid motion known as the itinerant oscillator[3] and for about 20 solutes in decalin solution was found to be proportional to the square of a model independent mean square volume of rotation V. The model was fitted to far infrared and microwave bandshapes using parameters K_0, K_1, and γ. The resulting plot of T_q vs V^2 revealed some interesting new features of molecular motion.

A further analysis by Reid,[2] based on microwave Debye relaxation times in a decalin solution, revealed that they were also proportional to V^2 to a good approximation. Such an analysis confirms the expectation that the Debye relaxation time is related to the low-frequency part of a spectrum whose second moment is the far infrared cross section. This second moment is the subject of a sum rule developed firstly by Gordon.[4] In absolute terms this sum rule does not produce quantitative agreement with the far infrared cross section. This was first reported by Pardoe *et al.*[1] and confirmed recently by Reid *et al.*[2] in a dilute decalin solution. The sum rule produces a value which is too low in comparison with experimental data. In some cases the discrepancy is very large. In a 10% tetrahydrofuran/decalin solution, for example, the theoretical Gordon value is only 31% of that observed, in furan/decalin 45%, in fluorobenzene/decalin 47%; while in more polar solutes such as methylene chloride the Gordon sum rule produces as much as 88% of the measured cross section.

This type of information is useful as regards the nature of molecular interactions in a common environment (decalin solvent) and many aspects remain to be clarified. In this paper we extend the analysis to the fourth spectral moment, i.e., $\int_0^\infty \bar{\nu}^2\alpha(\bar{\nu})d\bar{\nu}$, where $\bar{\nu}$ is the wave number and $\alpha(\bar{\nu})$ the optical power absorption coefficient.

THEORY

Following, for example, Böttcher and Bordewijk,[5] the relevant sum rules can be built up by expanding the orientational a.c.f. in a Taylor expansion with respect to $t=0$:

$$C_1(t)=\langle \mathbf{u}(t)\cdot\mathbf{u}(0)\rangle$$
$$=\sum_{n=0}^{\infty}\frac{t^n}{n!}\left[\frac{d^n}{dt^n}\langle \mathbf{u}(0)\cdot\mathbf{u}(t)\rangle\right]_{t=0}\ . \tag{1}$$

Classically, $C_1(t)$ is an even function of time, so that all odd derivatives should be zero. Therefore we have

$$C_1(t)=\sum_{n=0}^{\infty}(-1)^n\frac{t^{2n}}{(2n)!}\langle \mathbf{u}^{(n)}\cdot\mathbf{u}^{(n)}\rangle\ . \tag{2}$$

The sum rules of far infrared/microwave spectroscopy are now derived from the kinematic relation:

$$\dot{\mathbf{r}}_i=\boldsymbol{\omega}\times\mathbf{r}_i\ . \tag{3}$$

Here $\boldsymbol{\omega}$ is the angular velocity such that for any point in the molecule with distance $\mathbf{r}_i$ to the center of gravity the above relation holds.

For the derivatives $\mathbf{u}^{(n)}$ this yields

$$\dot{\mathbf{u}}=\boldsymbol{\omega}\times\mathbf{u}=\boldsymbol{\omega}_\perp\times\mathbf{u}\ ,$$
$$\ddot{\mathbf{u}}=\dot{\boldsymbol{\omega}}\times\mathbf{u}+\boldsymbol{\omega}\times\dot{\mathbf{u}}\ , \tag{4}$$

and so on.

If we define the moment of inertia $\mathbf{I}$ as a symmetric tensor given by

$$\mathbf{I}=\sum_i m_i(r_i^2\mathbf{1}-\mathbf{r}_i\mathbf{r}_i)\ , \tag{5}$$

the eigenvalues I_1, I_2, and I_3 of the moment of inertia are called the principal moments of inertia and the corresponding axes the axes of inertia.

The kinetic energy of the rotating body can be written as

$$W_{\text{kin}}=\frac{1}{2}\sum_i m_i\dot{r}_i^2=\tfrac{1}{2}\boldsymbol{\omega}\cdot\mathbf{I}\cdot\boldsymbol{\omega}$$
$$=\frac{1}{2}\sum_{i=1}^{3}I_i\omega_i^2\ , \tag{6}$$

where ω_i gives the component of the angular velocity along the axis of inertia with index i. Using Boltzmann statistics,

$$\langle\omega_i^{2n}\rangle=\frac{(2n)!}{n!}\left(\frac{kT}{2I_i}\right)^n\ , \tag{7}$$

which provides the well-known result

$$\tfrac{1}{2}I_i\langle\omega_i^2\rangle=\tfrac{1}{2}kT\ . \tag{8}$$

This equation makes it possible to calculate $C_1(t)$ up to

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terms in t^2. The principal axes of inertia of the molecule are the axes of the molecular coordinate system so that

$$\langle\dot{\mathbf{u}}\cdot\dot{\mathbf{u}}\rangle=\langle(\boldsymbol{\omega}\times\mathbf{u})\cdot(\boldsymbol{\omega}\times\mathbf{u})\rangle$$

$$=\langle\omega_1^2\rangle(u_2^2+u_3^2)+\langle\omega_2^2\rangle(u_1^2+u_3^2)+\langle\omega_3^2\rangle(u_2^2+u_3^2)\ , \tag{9}$$

$$=kT\left(\frac{u_1^2+u_2^2}{I_3}+\frac{u_1^2+u_3^2}{I_2}+\frac{u_2^2+u_3^2}{I_1}\right) \tag{10}$$

which is effectively the Gordon sum rule.[2] Note that there are no terms arising from molecular interaction.

Further terms in $C_1(t)$ can only be calculated with an expression for the time derivative of ω. Again, following Bordewijk and Bottcher, we define the angular momentum of the molecule by

$$\mathbf{J}=\boldsymbol{\omega}\cdot\mathbf{I}\ . \tag{11}$$

From this definition it follows that the angular momentum is related to the torque $\mathbf{T}_q$ on the molecule by

$$\dot{\mathbf{J}}=\sum_i m_i\,\mathbf{r}_i\times\ddot{\mathbf{r}}_i=\mathbf{T}_q\ . \tag{12}$$

In the molecule frame (moment of inertia coordinates), we have

$$\dot{\boldsymbol{\omega}}\cdot\mathbf{I}=\mathbf{T}_q-\boldsymbol{\omega}\times(\boldsymbol{\omega}\cdot\mathbf{I}) \tag{13}$$

so that

$$\begin{aligned}\ddot{u}_1&=\dot{\omega}_2+\omega_1\omega_3=T_2/I_2+\omega_1\omega_3[(I_2+I_3-I_1)/I_2]\ ,\\ \ddot{u}_2&=-\dot{\omega}_1+\omega_2\omega_3=-T_1/I_1+\omega_2\omega_3[(I_1-I_2+I_3)/I_1]\ ,\\ \ddot{u}_3&=-\omega_1^2-\omega_2^2\ .\end{aligned} \tag{14}$$

These equations give

$$\langle\ddot{\mathbf{u}}\cdot\ddot{\mathbf{u}}\rangle=\langle T_1^2\rangle/I_1^2+\langle T_2^2\rangle/I_2^2$$

$$+\frac{(kT)^2}{I_1^2I_2^2I_3}\left[\begin{matrix}I_3[8I_1I_2+I_3(I_1+I_2)]\\ +(I_1-I_2)^2(I_1+I_2+I_3)\end{matrix}\right] \tag{15}$$

which is a sum rule for the fourth spectral moment $\int_0^\infty\bar{\nu}^2\alpha(\bar{\nu})d\bar{\nu}$. Ignoring, for the sake of simplicity, internal field corrections we have

$$a_n=\langle\mathbf{u}^{(n)}\cdot\mathbf{u}^{(n)}\rangle$$

$$=\frac{2}{\pi(\epsilon_0-\epsilon_\infty)}\int_0^\infty\epsilon''(\omega)\omega^{2n-1}\,d\omega\ . \tag{16}$$

This equation holds when the dipole correlation function is equal to the step-response function of the orientational polarization (in the linear response region). The integral in this equation extends over the frequency range where the dielectric loss is due to the orientational polarization. With the further general relations

$$\alpha(\omega)=\omega\epsilon''(\omega)/n(\omega)c\ ,\quad \omega=2\pi\bar{\nu}c\ , \tag{17}$$

it is possible to obtain information about the torque term

$$\langle T_1^2\rangle/I_1^2+\langle T_2^2\rangle/I_2^2$$

from the integral $\int_0^\infty\bar{\nu}^2\alpha(\bar{\nu})d\bar{\nu}$, which is experimentally accessible using ultra-high-accuracy far infrared spectroscopy.

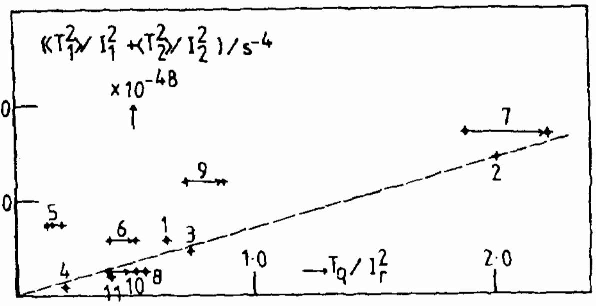

FIG. 1. A plot of 10^{-48} $(\langle T_1^2\rangle/I_1^2+\langle T_2^2\rangle/I_2^2)$ s^{-4} vs T_q/I_r^2 for 10% solution in decalin: (1) chloroform; (2) pyridine; (3) fluorobenzene; (4) pentafluorobenzene; (5) bromobenzene; (6) chlorobenzene; (7) toluene (20%); (8) nitrobenzene; (9) benzonitrile (5%); (10) 1-chloronaphthalene; (11) *t*-butyl chloride. For methylene chloride the ordinate value is 2.5 and the abscissa 11.7.

TABLE I. Measured a_n factors for solutes in decalin at 293 K.

Solute	ϵ_0	n_D	10^{-24} a_1/s^{-2} (± 10%)	10^{-48} a_2/s^{-4} (± 25%)	10^{-72} a_3/s^{-6} (± 50%)
CH_2Cl_2	2.59	1.405	9.29	3392	3.5×10^6
Fluorobenzene	2.47	1.468	3.70	494	1.4×10^5
Nitrobenzene	4.18	1.556	1.83	265	8.0×10^4
Chlorobenzene	2.46	1.524	5.23	590	1.5×10^5
Bromobenzene	2.50	1.560	7.34	747	1.9×10^5
Pentafluorobenzene	2.40	1.2	0.94	131	4.3×10^4
1-chloronaphthalene	2.43	1.63	1.64	239	9.2×10^4
t-butyl chloride	2.62	1.39	2.52	238	5.8×10^4
Pyridine	2.92	1.51	6.61	1442	8.6×10^5
Chloroform	2.36	1.45	3.50	660	3.9×10^5
(20%) Toluene	2.2	1.496	8.58	1740	6.4×10^5
(20%) Oxylene	2.27	1.51	···	···	···
(5%) Benzonitrile	3.00	1.56	7.51	1235	4.1×10^5

Similarly, sum rules can be developed for the orientational autocorrelation functions relevant to light scattering from molecules in solution and spin–spin NMR spectroscopy. This is,

$$C_2(t)=\tfrac{1}{2}\langle 3(\mathbf{u}(t)\cdot\mathbf{u}(0))^2-1\rangle \tag{18}$$

in the simplest case (i.e., neglecting cross-correlation and internal field corrections). This provides us with another expression involving $\langle T_1^2\rangle$ and $\langle T_2^2\rangle$ so that a pair of simultaneous equations is available, in principle, for $\langle T_1^2\rangle$ and $\langle T_2^2\rangle$ separately. This spectroscopic method of obtaining $\langle T_1^2\rangle$ and $\langle T_2^2\rangle$ could be checked using the results of molecular dynamics simulation, a theoretical method based on taking quite complicated expressions for the intermolecular potential energy. The analysis has been extended to the far infrared sixth moment by Evans.[6] This author has also suggested[7] that moment analysis of Rayleigh using spectra will provide us with model-independent information. Lastly we note that the above analysis is generally applicable to any asymmetric top, by definition dipolar. In the symmetric top, $\langle T_2^2\rangle$ vanishes if we write $T_\perp$ for the scalar value of the component of the resultant torque vector $\mathbf{T}_q$ perpendicular to $\mathbf{u}$.

TABLE II. Comparison of torque factors from moment and model analysis.

$10^{-48}\left(\frac{\langle T_1^2\rangle}{I_1^2}+\frac{\langle T_2^2\rangle}{I_2^2}\right)/\mathrm{s}^{-4}$	$10^{-38}\ T_q$	T_q/I_r^2	$10^{-40}\ I_1/\mathrm{g\ cm}^2$	$10^{-40}\ I_2/\mathrm{g\ cm}^2$	$10^{-40}\ I_3/\mathrm{g\ cm}^2$	Solute
2500	674	11701	26	256	277	CH_2Cl_2
600	990	624	252	252	500	$CHCl_3$
1396	1858	2016	140	145	285	Pyridine
484	2923	737	147	324	471	Fluorobenzene
100	3960	205	629	832	146	Pentafluorobenzene
745	2551 (3784)	130 (193)	147	820	967	Bromobenzene
586	3433 (4427)	389 (502)	147	530	677	Chlorobenzene
1730	6912 (8173)	1875 (2217)	152	325	477	Toluene
	9717 (11406)	1837 ( )	256	367	619	Oxylene
263	5932 (7878)	390 (518)	208	690	898	Nitrobenzene
1231	6781 (8173)	720 (867)	147	550	697	Benzonitrile
238	9786 (10647)	499 (543)	550	850	1400	1-chloronaphthalene
219	823 (1028)	402 (503)	191	286	286	*t*-butyl chloride

RESULTS

The decalin solutions chosen for reanalysis were those measured in the complete microwave/far infrared range by Reid and Evans.[2] In Table I we list some results for a_n of Eq. (16) for $n=1, 2, 3$. Except where stated the results refer to 10% v/v concentrations of each solute in decalin solvents at 293 K.

In Table I we list the a_n factors from Eq. (16), and in Table II we compare the torque factors derived from Eq. (15) with the model-dependent T_q factor of Reid and Evans. For direct comparison this has been divided by the square of I_r, the reduced moment of inertia defined by Reid *et al.*[2]

In Fig. 1 we plot the torque factor $\langle T_1^2\rangle/I_1^2+\langle T_2^2\rangle/I_2^2$ against T_q/I_r^2 for direct comparison. This is discussed below.

DISCUSSION

The abscissa and ordinate in Fig. 1 both represent estimates of torques derived from the same basic set of experimental data. The data should therefore fall into a straight line provided that the following assumptions are justifiable.

(i) Applicability of the sum rules, Eqs. (10) and (15), and neglect of internal field corrections.

(ii) The model assumptions[2] used in deriving T_q.

(iii) Averaging over I_1 and I_2 to produce I_r, the reduced moment of inertia.[2]

The values of T_q bracketed in Table II and arrowed in Fig. 1 are derived using the "torque-determined axes" method developed by Reid.[2] These provide a significantly better straight line in Fig. 1. About eight solutes torque values fall in a reasonably well defined line in Fig. 1, but there are some anomalies. Bromobenzene is above the line and methylene chloride below. There are several possible explanations for this, one being that the Gordon sum rule on a_1 (see, for example, Reid and Evans[2]) works much better for CH_2Cl_2/decalin than bromobenzene/decalin, possibly because the latter solute molecule is more weakly dipolar and more polarizable, so that a greater proportion of the experimental a_n may be collision induced. The sum rule for a_2 refers only to the motion of the permanent dipole so that any collision induced part will result in an over-estimation of the ordinates in Fig. 1. In CH_2Cl_2/decalin 88% of the observed a_1 is accounted for by Gordon sum rule. The equivalent proportion in bromobenzene is only 57%, and in benzonitrile (point 9 in Fig. 1) 66%. The mean for the other solutes in Fig. 1, excluding chloroform, is about 60%. The origin of the experimental excess over the sum rule values have been discussed by Reid and Evans.[2]

The third source of discrepancy in Fig. 1 arises from the necessity of using I_r to build up T_q/I_r^2. The ordinate is of course made up of two terms, $\langle T_1^2\rangle/I_1^2$ and $\langle T_2^2\rangle/I_2^2$, which cannot be considered separately without more information (from, for example, light scattering[7] or Raman spectroscopy). The derivations and meaning of I_r is discussed by Reid *et al.*[2]

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