INFLUENCE OF INTERMOLECULAR VIBRATIONAL RELAXATION IN LIQUIDS ON IR BANDSHAPES

P. C. M. VAN WOERKOM

STELLINGEN

I

De wijze waarop Döge zijn experimentele resultaten gebruikt ter rechtvaardiging van een op theoretische gronden te verwachten concentratie afhankelijkheid van de vibratiecorrelatiefunctie, is onjuist.

G. Döge, Z.für Natürforsch. 28a, 919 (1973)

II

De veronderstelling van Rothschild, dat bij de interpretatie van de Fouriertransforms van de IR absorptiebanden van een niet polaire vloeistof de vibratierelaxatie kan worden verwaarloosd als dit juist is voor een van de onderzochte bandvormen, is onjuist.

W.G.Rothschild, R.C.Livingston, J.J.Rush, J.Chem.Phys. 59, 2498 (1973)
Dit proefschrift.

III

De argumenten, die Mardaeva, Bondarev en Rusetsky gebruiken om de temperatuur onafhankelijkheid van enkele IR bandvormen toe te schrijven aan intermoleculaire vibratierelaxatie, zijn aan bedenkingen onderhevig.

A.I.Mardaeva, A.F.Bondarev, Yu.S.Rusetsky, Opt. i Spektr. 34, 1088 (1973)
Dit proefschrift.

IV

De wijze, waarop Bartoli en Litovitz IR correlatiefuncties scheiden in onafhankelijke vibratie- en rotatierelaxatiefuncties, kan in vele gevallen aanleiding geven tot fouten in de interpretatie van IR bandvormen.

F.J.Bartoli, T.A.Litovitz, J.Chem.Phys. 56, 404,413 (1972)
Dit proefschrift.

V

De betrouwbaarheid van IR correlatiefuncties is aanzienlijk beter als algemeen wordt aangenomen op grond van de foutendiscussie gegeven door Fujiyama en Crawford.

T.Fujiyama. Br.Crawford Jr. J.Phys.Chem. 73, 4040 (1969)
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VI

Het hoge percentage erythro dibromide bij de bromering van Z-β-tBu styreen in CCl_4 wordt waarschijnlijk mede veroorzaakt door een tijdens de reactie optredende Z-E isomerisatie.

R.J.Abraham, J.R.Monasterios, J.Chem.Soc. Perkin I, 14, 1446 (1973)
W.J.Muizebelt, Dissertatie Nijmegen (1967)

VII

Een aantal resultaten van Godin en Wan Ng betreffende dissociatieconstantes voor de kation gestimuleerde opname van TNBS in eiwitten van erythrocyte membranen is aan bedenkingen onderhevig.

D.V.Godin, T.Wan Ng, Molec.Pharm. 8, 426 (1972)

VIII

De door Alberty en Miller gegeven geintegreerde snelheidsvergelijking voor A in het geval van een cyclische reactie tussen de componenten A, B en C, waarbij alleen de reactie tussen A en B reversibel is en de beginconcentraties van B en C nul zijn, is onjuist.

R.A.Alberty, W.G.Miller, J.Chem.Phys. 26, 1231 (1957)

IX

Theoretische beschouwingen over de zelfdiffusieconstante D van tegenionen in polyelectrolyt-oplossingen worden gewoonlijk gehouden over een anisotroop systeem van evenwijdig geplaatste polyelectrolyt-"staven". De door Pefferkorn en Varoqui voorgestelde correctie van de zo gevonden waarde voor D, om de isotropie van een reëele oplossing in rekening te brengen, is in strijd met de opvatting dat de gemiddelde waarde van het kwadraat van de verplaatsing van een diffunderend deeltje recht evenredig is met de tijd (voor niet zeer kleine tijden).

E.Pefferkorn, R.Varoqui, Eur. Polym.J. 6, 663 (1970)

X

Het verdient aanbeveling om dienstplichtigen, die door studieuitstel op oudere leeftijd onder dienst gaan, te onderwerpen aan een aanzienlijk uitgebreidere medische keuring dan nu gebruikelijk is. Dit met name in verband met de verontrustende toename van hart- en vaatziekten onder jonge mensen.

XI

Het verdient aanbeveling reclame ter bevordering van de preventie van hart- en vaatziekten zodanig te presenteren, dat de geestelijke gezondheid van hartpatienten er niet onder lijdt.

P.C.M. van Woerkom 20 maart 1974

De promotie zal plaatsvinden in de Senaatskamer van het Academiegebouw, Rapenburg 73 te Leiden.

Tot de promotie wordt met het oog op de beperkte ruimte in de Senaatskamer uitsluitend toegang verleend op vertoon van een uitnodiging.

RECEPTIE NA AFLOOP VAN DE PROMOTIE
(17.15 uur)
IN HET ACADEMIEGEBOUW

U wordt er op geattendeerd dat het moeilijk en tijdrovend is om in de omgeving van het Academiegebouw te parkeren.

INFLUENCE OF INTERMOLECULAR VIBRATIONAL RELAXATION IN LIQUIDS ON IR BANDSHAPES

PROEFSCHRIFT

ter verkrijging van de graad van Doctor
in de Wiskunde en Natuurwetenschappen
aan de Rijksuniversiteit te Leiden,
op gezag van de Rector Magnificus
Dr. A.E.Cohen, Hoogleraar in de faculteit
der Letteren, volgens besluit van het
college van dekanen te verdedigen
op woensdag 20 maart 1974
te klokke 16.15 uur

door

PETRUS CORNELIS MARIA VAN WOERKOM

geboren te Tilburg in 1947

Krips Repro B.V. Meppel

PROMOTOR: DR. J.C. LEYTE

Aan mijn ouders

Aan Hetty

CONTENTS

CHAPTER I

INTRODUCTION

1. GENERAL REMARKS

IR bandshapes of liquids contain information about molecular motion and intermolecular interaction. The width at half intensity and the frequency shift of the bandmaximum with respect to the frequency in the vapor phase have been investigated to estimate the influence of these factors on the spectra of liquids (1-19). Furthermore the study of the integrated absorption intensity may be useful in this context (16-18).

A more recent method to obtain information about molecular motions and intermolecular interactions is the Fouriertransformation of IR absorption bands (20-36). In this way information about the dipole moment correlation function $\Phi(t)$ is obtained. $\Phi(t)$ can be written as (37)

$$\Phi(t)=\tfrac{1}{2}\left\langle\left[\vec{M},\vec{M}(t)\right]_+\right\rangle=\tfrac{1}{2}\left\langle\left[\vec{M},\vec{M}\right]_+\right\rangle\frac{\int_{-\infty}^{+\infty}d\omega\ \mathrm{cotgh}(\tfrac{1}{2}\beta\hbar\omega)n(\omega)k(\omega)\cos\omega t}{\int_{-\infty}^{+\infty}d\omega\ \mathrm{cotgh}(\tfrac{1}{2}\beta\hbar\omega)n(\omega)k(\omega)} \qquad (1)$$

in which $\vec{M}$ is the total dipole moment of the system, ω the frequency (in rad.sec^{-1}) and $n(\omega)$ and $k(\omega)$ are the real and imaginary parts of the complex refractive index. The brackets $[\ ]_+$ indicate an anticommutator, the brackets $\langle\ \rangle$ indicate the averaging procedure, $\beta=(kT)^{-1}$ and h is Planck's constant. Usually the frequency ω_0 of the bandmaximum of an investigated absorption band is chosen as frequency zero. The normalized time correlation function C(t)

obtained in this way is given by

$$C(t)=\frac{\int_{-\infty}^{+\infty} d\omega \ \mathrm{cotgh}(\tfrac{1}{2}\beta\hbar\omega)n(\omega)k(\omega)\cos\{(\omega-\omega_0)t\}}{\int_{-\infty}^{+\infty} d\omega \ \mathrm{cotgh}(\tfrac{1}{2}\beta\hbar\omega)n(\omega)k(\omega)} \tag{2}$$

The optical constant $k(\omega)$ is proportional to $\alpha(\omega)\omega^{-1}$ (31) ($\alpha(\omega)$ is the molar extinction coefficient at frequency ω which can be obtained from IR absorption bands). At sufficiently high frequency $\mathrm{cotgh}(\tfrac{1}{2}\beta\hbar\omega)$ is an insensitive function of ω and in that case $C(t)$ is proportional to the cosine transform of $n(\omega)k(\omega)$. For IR absorption bands it will usually be justified to neglect the frequency dependence of $\mathrm{cotgh}(\tfrac{1}{2}\beta\hbar\omega)$.

Often $n(\omega)$ is not taken into account and it is supposed that the cosine transform of $k(\omega)$ yields the dipole moment correlation function (38). However, as pointed out by Fulton (37), the dipole moment correlation function is related to the Fouriertransform of the complex dielectric constant $\hat{\varepsilon}(\omega)$. Using the relation between $\hat{\varepsilon}(\omega)$ and $\hat{n}(\omega)$, the complex index of refraction, it can easily be shown that the cosine transform of $n(\omega)k(\omega)$ yields the correct correlation function. Neglect of the frequency dependence of $n(\omega)$ introduces considerable errors in the dipole moment correlation function in many cases.

Especially those IR absorption bands which are isolated from other bands in the spectrum are suitable for investigation by Fouriertransformation. The macroscopic dipole moment correlation function obtained in this way is determined by the rotational and vibrational behavior of the molecules in the liquid; the loss of correlation is due to rotational and vibrational relaxation.

Rotational relaxation is caused by the reorientation process of the molecules in the liquid. The directions of all microscopic moments which are rigidly determined by the orientation of the molecular frame will change in time. This obviously results in a loss of correlation for the macroscopic dipole moment.

Vibrational relaxation affects only the oscillating part of the

total dipole moment, which is due to the intramolecular vibrations in the liquid. This relaxation mechanism causes the finite lifetime of an excited vibrational state (e.g. due to de-excitation and energy transfer).

In the case of an isolated IR absorption band at frequency ω_0 the cosine transform according to eqn.(2) is mainly determined by the part of the total dipole moment which is oscillating with frequency ω_0. Usually the microscopic transition dipole moments which contribute to the total electric moment are assumed to be mutually uncorrelated if localized on different molecules. Using this assumption the time correlation function may be interpreted in terms of the average time evolution of a molecular transition dipole moment. The interpretation of the correlation functions is, however, complicated because the separation of the rotational and vibrational relaxation contributions is generally not possible exactly. This point will be amplified in this thesis.

Different methods have been developed to perform this separation approximately. These methods (9,40,41) are reviewed in section 3 of this chapter together with the main experimental results obtained from IR bandshape studies. In section 2 the most important theories concerning IR bandshapes are reviewed.

2. REVIEW OF IR BANDSHAPE THEORIES

One of the first authors who has discussed vibrational spectra in terms of correlation functions was Sobelman (39). It was argued that depolarized Raman lines are dependent on time correlation functions describing the rotational behavior of the molecules.

A more detailed theoretical approach of both Raman and IR bandshapes in terms of time correlation functions has been presented by Gordon (38,42,43). The discussion of Gordon's treatment is confined here to its description of IR bandshapes.

The interpretation of IR correlation functions by Gordon is

based on the assumption that the lifetime of an excited vibrational state is infinite compared with the time scale of interest for dipole moment correlation functions (0-3 psec.). In fact the vibrational relaxation is neglected. In this way the dipole moment correlation functions are interpreted completely in terms of the rotational motions of the molecules.

The short time behavior of the correlation function reflects the free rotation behavior of the molecules in liquids. Gordon has treated this behavior by an expansion in powers of t of the correlation function. For short times the first terms of this expansion may give a reasonable description of the decay of the correlation function. The coefficients of this time series have been related to equilibrium properties of the molecular system under investigation. For instance the coefficient of the t^2 term has been related to the rotational kinetic energy of a free rotor.

At longer times, when collisions randomize the orientation of the transition dipole moment a stochastic model has been used for the interpretation of the correlation function. Gordon has treated the long time behavior in terms of the rotational diffusion model. In this way IR bandshape studies may be used to determine rotational diffusion constants.

However, the description of IR correlation functions by rotational relaxation only is insufficient in many cases. Therefore several attempts have been performed to treat the correlation functions in such a way that vibrational relaxation can be taken into account (40,41,44-46). Two approaches will be reviewed here; the theories of Bratos et al.(44) and Morawitz et al.(46). Because the treatment of Bratos is most widely used in the literature and discusses many aspects of dipole moment correlation functions a fairly detailed description of this theory will be given here.

The theory of Bratos is concerned with IR spectra of diatomic molecules in inert solvents. The system is composed of one IR active molecule surrounded by a large number of nonabsorbing inert solvent molecules. The vibration of the IR active molecule is anharmonic and is modulated by a stochastic potential $V_s(r,t)$ due to

the surrounding solvent molecules. The parameter r in $V_s(r,t)$ describes the dependence of the potential on the vibrational coordinate.

Bratos has simplified the treatment by a few basic assumptions. The total dipole moment of the molecule consists of two parts; the permanent and transition dipole moment. Induced moments due to other processes in the liquid have been neglected. Furthermore, there is no vibration-rotation coupling. This implies that the intramolecular vibrational degree of freedom and the molecular reorientation are uncorrelated. The molecular reorientation has been described by a stochastic model, which is a classical treatment. In contrast with this the intramolecular vibration has been described quantummechanically. Therefore the theory of Bratos is semiclassical. The liquid has been assumed to be isotropic and the incident lightbeam is non-polarized.

The treatment starts from the following expression for the dipole moment correlation function $\Phi_c(t)$,

$$\Phi_c(t)=\left\langle \vec{M}\,\vec{M}(t)\right\rangle \tag{3}$$

in which $\vec{M}(t)$ is the Heisenberg representation of the dipole moment operator $\vec{M}$ as in eqn.(1). The subscript c indicates that contrary to the definition of the correlation function in eqn.(1) the classical definition of the correlation function is used by Bratos.

The function $\Phi_c(t)$ is separated into a product of two time correlation functions. This has been performed by writing $\vec{M}(t)$ in the following form;

$$\vec{M}(t)=M(t)\vec{u}(t) \tag{4}$$

in which M(t) is the length of the dipole moment vector and $\vec{u}(t)$ is the unit vector describing the orientation of the dipole moment.

Using the assumption that the vibrational and rotational motion of the IR active molecule are uncorrelated and averaging independently over the vibrational coordinate and over the stochastic variables

Bratos obtains the following expression for $\Phi_c(t)$,

$$\Phi_c(t)=\left\langle \mathrm{Tr}\rho_0 M\, M(t)\right\rangle_s \left\langle \vec{u}\,\vec{u}(t)\right\rangle_s \tag{5}$$

where ρ_0 is the vibrational density matrix. $\mathrm{Tr}\rho_0$ indicates the averaging over the vibrational coordinate (quantummechanically) and the brackets $\langle\rangle_s$ indicate the averaging over the stochastic variables.

At this point the vibrational correlation function $\Phi_v(t)$ and the rotational correlation function $\Phi_r(t)$ are defined;

$$\Phi_v(t)=\left\langle \mathrm{Tr}\rho_0\, M\, M(t)\right\rangle_s \tag{6a}$$

$$\Phi_r(t)=\left\langle \vec{u}\,\vec{u}(t)\right\rangle_s \tag{6b}$$

Using these definitions $\Phi_c(t)$ is written as

$$\Phi_c(t)=\Phi_v(t)\Phi_r(t) \tag{7}$$

Eqn.(7) shows explicitly the most important assumption of this theory already made in deriving eqn.(5); the independence of the rotational and vibrational relaxation. On the basis of this equation the majority of the experimental data from IR bandshape studies have been discussed. Notwithstanding the fact that Bratos' treatment is concerned with diatomic molecules in inert solvents eqn.(7) is used to interpret the spectra of both solutions and pure liquids.

An expression for the vibrational correlation function $\Phi_v(t)$ has been calculated using the Kubo theory on lineshape and relaxatión (47). The excited vibration is treated in this way as a randomly modulated oscillator; the fluctuation of the vibrational frequency is considered to be a random process. In such cases the nature of the modulation process determines the time dependence of $\Phi_v(t)$. For dilute solutions Bratos assumes that translational diffusion is the most important relaxation mechanism for $\Phi_v(t)$. In other words, the perturbation of the vibrational frequency is modulated by the translational diffusion. In this case the ratio of τ_t (the

translational diffusion time which characterises the rate of change of the surroundings for the excited oscillator) and $(\Delta\omega_v)^{-1}$ (lifetime of an excited vibration) determines the behavior of $\Phi_v(t)$.

If $\Delta\omega_v\tau_t \ll 1$ the system is in the fast modulation limit. An exponential decay for $\Phi_v(t)$ is then expected for $t \gg \tau_t$. If on the other hand $\Delta\omega_v\tau_t \gg 1$ the perturbation is treated in the slow modulation limit. This results into a Gaussian decay for $\Phi_v(t)$ if the perturbation is a Gaussian process. For other types of perturbations the solution of $\Phi_v(t)$ will be complicated. In Bratos' treatment the slow modulation limit is considered. This is, together with eqn.(7), the most important assumption of this theory.

Using the Kubo theory an expression for $\Phi_v(t)$ is derived. Systems are considered where only the vibrational ground state is populated. For a 0-α transition $\Phi_v(t)$ is given by

$$\Phi_v(t)=\Phi_v(0)\exp\left[-i\langle\omega_{0\alpha}(0)\rangle_c t + \tfrac{1}{2}i^2\langle\omega_{0\alpha}^2(0)\rangle_c t^2 - \cdots\cdots\right] \qquad (8)$$

The brackets $\langle\ \rangle_c$ indicate the cumulant averages (47). The function $\omega_{0\alpha}(0)$ is the random perturbation of the vibrational frequency in which (0) means that the time dependence is suppressed due to the fact that the slow modulation limit is considered.

However, eqn.(8) is generally not suitable for a detailed calculation of $\Phi_v(t)$, because of the fact that many terms of the expansion must be included. Only if the perturbation is a Gaussian process $\Phi_v(t)$ can be written in a more simplified form. In this case the first two terms of the expansion are important and higher order terms may be neglected. Still, even the calculation of these terms is complicated.

The rotational correlation function $\Phi_r(t)$ is treated by using a stochastic model. Three cases are distinghuished; free rotation, rotational diffusion and an intermediate case of free rotation and rotational diffusion (44).

Combining one of the resulting rotational correlation functions with the vibrational correlation function, a theoretical expression for $\Phi_c(t)$ is obtained. The expressions for $\Phi_c(t)$ are then used to

calculate theoretical IR bandshapes by Fouriertransformation.

Finally it is interesting to note that it is assumed that vibrational relaxation is temperature independent. This implies that the temperature dependence of $\Phi_c(t)$ originates from the rotational correlation function. It is this assumption which is of major importance in connection with a well-known experimental method developed to separate approximately the vibrational correlation function from the rotational correlation function (9,40). This will be discussed in section 3 of this chapter.

The most striking feature of the Bratos theory (and of nearly all IR bandshape theories) is the complete neglect of the possibility that vibrational relaxation may depend on the rotational motions of the molecules. This is remarkable because the intermolecular interactions depend in principle on the relative orientation of the interacting molecules. Especially when vibrational relaxation due to intermolecular interactions is important, it is reasonable to expect that the neglect of the influence of the reorientation of the molecules on the vibrational relaxation is not justified. This implies furthermore, that the separation of $\Phi_c(t)$ as in eqn.(7) is unjustified.

The theory of Morawitz and Eisenthal (46) is a second example of a treatment including vibrational relaxation. The investigated liquid model consists of a large number of identical molecules. For the sake of simplicity each molecule contains only one internal degree of freedom (one intramolecular vibration). The Hamilton operator for the system has been defined in such a way that the molecular motion is described in terms of coupled rotational-translational degrees of freedom. Furthermore, the Hamilton operator contains a term representing the coupling between the IR active vibration and the rotational-translational degrees of freedom. This coupling term causes a frequency shift and a broadening of the bandshape.

Physically the interactions between the molecules in the liquid, which determine the time dependence of the dipole moment correlation functions, are considered to be collision processes. From this point of view, the rotational-translational part of the Hamiltonian describes dephasing (soft) collisions. These collisions reorient the

molecules without de-excitation of the vibrations. The interaction between the rotational-translational degrees of freedom and the intramolecular vibrations causes vibrational relaxation (energy transfer and de-excitation). This is considered to be the result of strong collisions.

Morawitz and Eisenthal assume that the relaxation processes due to soft and strong collisions can be separated. This implies the assumption that vibrational relaxation does not depend on rotational relaxation. Finally the following result for $\Phi_c(t)$ has been obtained

$$\Phi_c(t)=\Phi_r(t)\Phi_v(0)e^{-\gamma|t|} \tag{9}$$

in which γ is the reciprocal vibrational correlation time.

Analogous to the treatment of Bratos the dipole moment correlation function has been written in a product of the rotational correlation function and an independent vibrational correlation function. In the treatment of Morawitz the vibrational correlation function shows an exponential decay, however, contrary to the result obtained by Bratos.

Several other theoretical contributions to the subject of IR bandshapes have been published (3,48,49). Especially the theory of Valiev (49) is important here. Valiev gives a calculation of the contribution of the transition dipole-transition dipole coupling to the halfwidth of an absorption band. This mechanism may be responsible for the resonant transfer of vibrational energy between identical oscillators in liquids, which is an example of intermolecular vibrational relaxation. As the subject of the present study is intermolecular vibrational relaxation due to interoscillator coupling, it is of interest to describe the calculation of Valiev in some detail here.

The contribution of the transition dipole-transition dipole coupling to the halfwidth $\Delta\omega_{\frac{1}{2}}$ (in rad.sec^{-1}) has been obtained using the relation

$$\Delta\omega_{\frac{1}{2}} = \frac{1}{\hbar}\left[\left\langle G_{dip}^{2}\right\rangle\right]^{\frac{1}{2}} . W_{st} \tag{10}$$

where G_{dip} is the transition dipole-transition dipole interaction. The brackets indicate the averaging procedure over the molecular orientations. The factor W_{st} in eqn.(10) has been defined to be the probability that one of the two interacting oscillators is in an excited vibrational state; in fact this takes into account the population of vibrational energy levels.

The coupling between non-identical oscillators in the system has been neglected in the calculation. After performing the averaging procedure in eqn.(10), the following expression has been obtained

$$\Delta\omega_{\frac{1}{2}} = \frac{\left(\frac{\partial\mu}{\partial Q}\right)^{2}}{3\omega_0}\left[\frac{2\pi N}{d^3}\right]^{\frac{1}{2}} . W_{st} \tag{11}$$

In eqn.(11) μ is the dipole moment, Q the normal coordinate, ω_0 is the vibration frequency, N the number density of identical oscillators and d represents the distance of closest approach between two oscillators. It should be borne in mind that the expression obtained for $\Delta\omega_{\frac{1}{2}}$ is independent on the molecular reorientation. As shown by Valiev, eqn.(11) predicts values of $\Delta\omega_{\frac{1}{2}}$, which indicate that transition dipole-transition dipole interaction has a negligible influence on the halfwidth of an IR absorption band.

However, as pointed out by Fujiyama (3), realistic values for $\Delta\omega_{\frac{1}{2}}$ can be obtained by ommitting the factor W_{st}. It is argued by this author that it is only necessary to take into account the probability that an excited vibration can transfer its vibrational energy. Obviously this probability is nearly equal to unity.

Recently it has been pointed out (48,23) that intermolecular vibrational relaxation due to transition dipole-transition dipole coupling should depend on the molecular reorientation. A detailed treatment of this dependence will be presented in this thesis.

3. REVIEW OF EXPERIMENTAL DATA

The work of Gordon (38) on dipole moment correlation functions is used by many authors to discuss their experimental data (4,26-29, 32-36). For instance, Crawford et al.(26,27,34) have discussed dipole moment correlation functions completely in terms of the molecular reorientation. Absorption bands of C_6F_6, CH_3J and CD_3J have been interpreted in this way. The long time behavior of the obtained dipole moment correlation functions has been discussed in terms of the rotational diffusion model. At short times the decay is Gaussian and can be used to determine angles of free rotation before the molecules in the liquid undergo collisions. In this way Rothschild (32) has determined the rotational diffusion tensor of CH_2Cl_2 using the assumption that all investigated fundamental absorptions of CH_2Cl_2 can be discussed in terms of molecular reorientation. Furthermore, the influence of molecular association on the rotational behavior has been investigated (33,36). In rather weakly associating systems, such as $CHCl_3$ - C_6H_6 solutions, no influence on the dipole moment correlation function was found.

It has been stressed by Crawford and coworkers (27) that the dipole moment correlation functions are very unreliable at longer times. This has been concluded on the basis of a detailed estimation of errors (such as truncation and baseline effects). Therefore it is usually assumed that especially the short time behavior of the correlation functions is the most interesting part to study, because this part may be known accurately. In chapter II of this thesis it will be pointed out that Crawford's result is incorrect.

Although the results obtained by interpreting the data according to Gordon's theory are interesting, it has been stressed by several authors that the interpretation of IR correlation functions in terms of reorientational motions can be very complicated (25,30,31). These problems are due to experimental errors (31) and processes occuring in the liquid (25) which influence the bandshape considerably (e.g. vibrational relaxation) .

As pointed out by Young and Jones (31) IR transmission measurements may be obscured by interference and reflection loss distortion. Especially strongly absorbing liquids, which have to be measured as thin films, give rise to large problems even when thin films of high accuracy have been constructed. Detailed criteria have been given by Young and Jones, which indicate under what circumstances significant disturbances of the spectrum will arise.These criteria have been presented in terms of the magnitude of the optical constant $k(\omega)$ and the path length of the liquid cell used in the experiment.

A paper considering the possible influence of several physical processes in the liquid on dipole moment correlation functions has been published by van Konijnenburg and Steele (25). It has been shown that before dipole moment correlation functions can be interpreted in terms of molecular reorientations contributions due to other processes have to be removed. Possible cooperative behavior of the molecules and collision-induced effects have to be taken into account. Furthermore the existence of isotopic species (e.g. ^{35}Cl and ^{37}Cl) and hot bands may influence the absorption band in an important way. A method to correct for these effects has been given. Vibrational relaxation has been neglected by van Konijnenburg, although many authors have pointed out that this relaxation mechanism is important (3,23,30,40,48).

In this context it is clear that the separation of the vibrational and rotational contributions is one of the main difficulties in the interpretation of IR bandshapes. Two methods have been developed to obtain the rotational and vibrational contributions to IR bandshapes separately (9,40).

The first approach was developed by Rakov (9) and has been extended recently by Bartoli and Litovitz (40). Here, temperature independence of the vibrational relaxation is assumed. From the IR bandshape at low temperature, the intrinsic vibrational linewidth is determined. This intrinsic linewidth is then used to determine the reorientational linewidth at higher temperatures by subtracting from the whole bandwidth at a given temperature the intrinsic width. This method is only applicable if the bandshape is Lorentzian (or

nearly Lorentzian) over a large temperature range. It has to be stressed that the additivity of the rotational and vibrational contributions to the linewidth is only justified if vibrational relaxation is independent of the rotational relaxation.

Because IR bandshapes are never exact Lorentzians it is clear that the Rakov method has large limitations. Therefore, attention has been focused recently on another approach discussed by several authors (40,41,50). The only assumption included here is the independence of rotational and vibrational relaxation. Using this method the vibrational lineshape is obtained from Raman scattering data. Therefore the applicability of the method is confined to IR active vibrations which are also Raman active. Fouriertransformation of Raman bands yields information about the correlation functions for the elements of the polarizability tensor (40,41). The correlation function of the isotropic part of the polarizability tensor obtained in this way is independent on the reorientation of the molecules and is assumed to be the vibrational correlation function both for the IR correlation function and the correlation function of the anisotropic part of the polarizability tensor. The vibrational correlation function can then be used to extract from the IR correlation function the reorientational correlation function. However, until now this method is scarcely used to correct IR correlation functions. It will be pointed out in this thesis that both the Rakov and the Raman method are incorrect.

A considerable amount of experimental results concerning correlation functions, both from IR spectra and Raman spectra, have been discussed using the two preceding methods (40,48,50-54). Using the Raman method Raman scattering measurements have shown that the vibrational correlation function can be temperature dependent (48,51, 54). This is in contradiction to the usual assumption that vibrational relaxation is temperature independent. Concerning the vibrational relaxation several mechanisms have been proposed; e.g. vibrational energy transfer between molecules (resonance broadening), molecular association and electrostatic interactions (3,48,49,55).

With respect to the present study vibrational energy transfer

is the most important mechanism. Transfer of vibrational energy between identical oscillators in the liquid may occur due to an electrostatic interaction between these oscillators.An example of such a coupling is the transition dipole-transition dipole interaction, as discussed by Valiev (49). Experimentally this relaxation mechanism may be investigated by comparing IR bandshapes of pure liquids with corresponding bands in isotopically diluted solutions (1,23,54). It is then assumed that diminishing of the probability of resonant transfer is the only change on dilution, while other relaxation mechanisms remain unchanged. Inert solvents and solvents which have the same molecular volume and dipole moment as the investigated pure liquid have also been used (2,56).

4. OUTLINE OF THE PRESENT STUDY

As pointed out in the previous sections, it is generally assumed that the dipole moment correlation function obtained from an IR absorption band can be written as a product of two independent correlation functions. These functions are called the rotational and the vibrational correlation function. The vibrational correlation function is usually defined in such a way that it contains all contributions to the IR bandshape which are not of a purely reorientational character. However, as already noted in section 2, it seems reasonable to expect that when intermolecular vibrational relaxation is important the assumption of the independence of vibrational and rotational relaxation can not be justified.

In view of this, intermolecular vibrational relaxation due to the coupling between identical oscillators is the main subject of this study. Using the isotopic dilution method (23) the influence of the interoscillator coupling on IR correlation functions has been investigated for several systems. Also dilution series in other solvents have been performed. In this way it is possible to demonstrate that the isotopic dilution method is the most suitable one for the investigation of interoscillator coupling. Furthermore the temperature

dependence of the isotopic dilution effect has been measured. The experimental data are presented in Chapter III.

Before presenting the experimental results, a detailed discussion of the method used and its reliability is given in Chapter II.

A theory describing the transition dipole correlation functions will be given in Chapter IV. This treatment is based on the linear response formalism, as presented by Kubo (57). An expression for the transition dipole correlation function has been derived which is suitable for calculating the effect of intermolecular interactions on IR bandshapes. In this way it is shown that the transition dipole-transition dipole coupling may account for the observed isotopic dilution effect. Both the magnitude and the temperature dependence of the theoretically predicted effect are in reasonable agreement with the experimental data. This is pointed out in Chapter V, where a comparison between theory and experiment is given together with a review of the obtained results. It is then concluded that vibrational relaxation is generally not independent on the reorientational behavior of the molecules.

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CHAPTER II

EXPERIMENTAL TECHNIQUE

1. THE METHOD

The investigation of intermolecular vibrational relaxation has been performed by using the isotopic dilution method (1). The IR bandshape of a neat liquid is compared with the bandshape of the same compound in isotopically diluted solutions. On dilution the most important change of the environment of the investigated molecules is due to a shift of the frequencies of the surrounding oscillators. It may be expected that the microdynamical behavior of the molecules is unchanged. In this way the influence of intermolecular vibrational relaxation on IR absorption bands can be studied in favorable cases.

As pointed out before (1), it is necessary that an absorption band is isolated from other absorptions in the spectrum. This condition will be met readily if over a frequency range of about ten times the width at half intensity no other absorptions are found. This experimental condition implies that the isotopic dilution method is only applicable to a limited number of absorption bands.

The spectra have been recorded using a PE-325 doublebeam spectrophotometer. The spectral resolution was about 0.5 cm^{-1}, and the spectra were recorded with a scanning speed of about 1 cm^{-1}/min. KBr windows separated by a lead spacer have been used to construct appropriate liquid cells. Using a variable path length cell in the reference beam the spectra were corrected for solvent absorption. The temperature during the measurements was kept constant to within $1^{o}C$.

From the experimentally obtained IR transmission data dipole

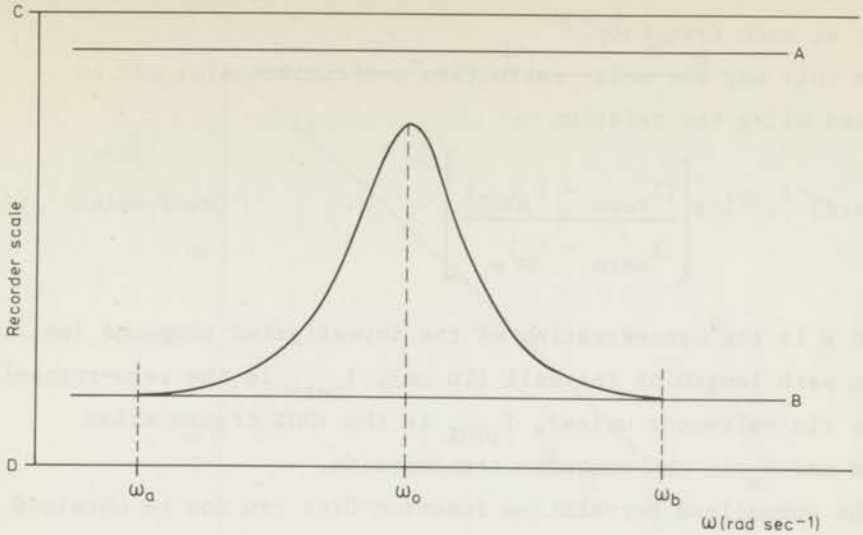

Fig.1. A possible result of an IR transmission measurement.

moment correlation functions have been calculated using a computer program (2). The calculation may be illustrated by Fig.1 which shows a possible result as obtained from an IR transmission measurement. The frequency unit has been given in rad.sec^{-1}. The distance CD marks the span of the recorder. The transmission values of the bandshape are recorded on punched paper tape using a digital voltmeter (Solartron LM 1450) connected to the slave recorder output. The digital voltmeter has a 3½ digit display. The density of punched values is 4 per wavenumber for all measurements, except for the absorption band of $CDCl_3$ at 910 cm^{-1} where the sampling density is 10 per wavenumber. Furthermore the position of the zero-transmission line (line A in Fig.1) has been determined in voltmeter units. The value of the 100% transmission position in voltmeter units is obtained by choosing two frequencies (ω_a and ω_b in Fig.1) as far as possible in the wings, which define the integration interval. The line connecting the transmission values at these frequencies is used as the 100% transmission line (line B in Fig.1). An interpolation procedure in the computer program gives the 100% transmission

position at each frequency.

In this way the molar extinction coefficient $\alpha(\omega)$ can be calculated using the relation

$$\alpha(\omega) = (x.d)^{-1}.{}^{10}\log\left[\frac{(I_{zero} - I_{100\%})_\omega}{(I_{zero} - I_m)_\omega}\right] \qquad (\alpha(\omega) \sim \omega k(\omega)) \quad (1)$$

in which x is the concentration of the investigated compound ($mol.l^{-1}$), d is the path length of the cell (in cm), I_{zero} is the zero-transmission position (in voltmeter units), $I_{100\%}$ is the 100% transmission position and I_m is the measured transmission.

The normalized correlation function C(t) can now be obtained using the following expression

$$C(t) = \frac{\sum_i \{\alpha(\omega_i)\cos\{(\omega_i - \omega_0)t\} + \alpha(\omega_{i+1})\cos\{(\omega_{i+1} - \omega_0)t\}\}\Delta\omega}{\sum_i \{\alpha(\omega_i) + \alpha(\omega_{i+1})\}\Delta\omega} \qquad (2)$$

In eqn.(2) $\Delta\omega$ is the frequency difference between succeeding punched transmission values, ω_0 is the frequency at which $\alpha(\omega_i)$ reaches its maximum value and the summation extends over all recorded values of the integration interval chosen (between ω_a and ω_b).

Furthermore the integrated intensity of the absorption band is calculated.

If necessary it is also possible to take into account the refractive index (3). Then $\alpha(\omega_i)$ in eqn.(2) has to be replaced by $\alpha(\omega_i)n(\omega_i)$. The refractive index has been measured using an interferometric method. However, the variation of the refractive index over the absorption band has turned out to be negligible in nearly all measured spectra. Only the dipole moment correlation function obtained from the absorption band of $CDCl_3$ at 910 cm^{-1} changes significantly if this correction is applied. This is illustrated by Fig.2 and 3, where for $CHCl_3$ (absorption band at 1215 cm^{-1}) and $CDCl_3$ (at 910 cm^{-1}) lnC(t) is shown both with and without the correction for the frequency dependence of the refractive

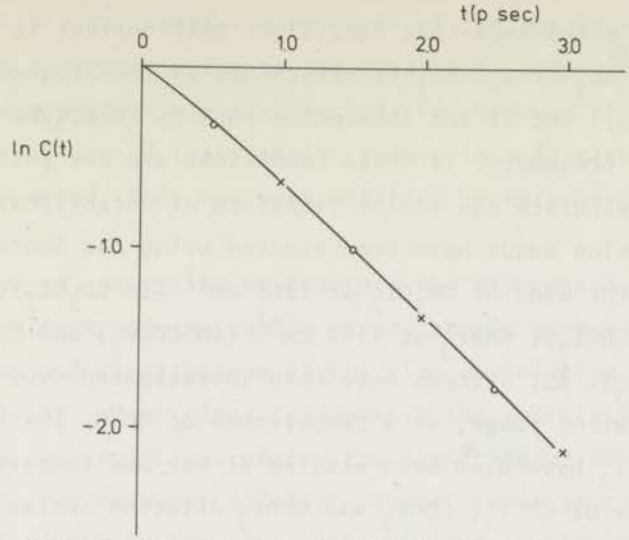

Fig.2. Ln C(t) for the absorption band of $CHCl_3$ at 1215 cm^{-1}.
×: taking into account the frequency dependence of n(ω).
o: neglecting the frequency dependence of n(ω).

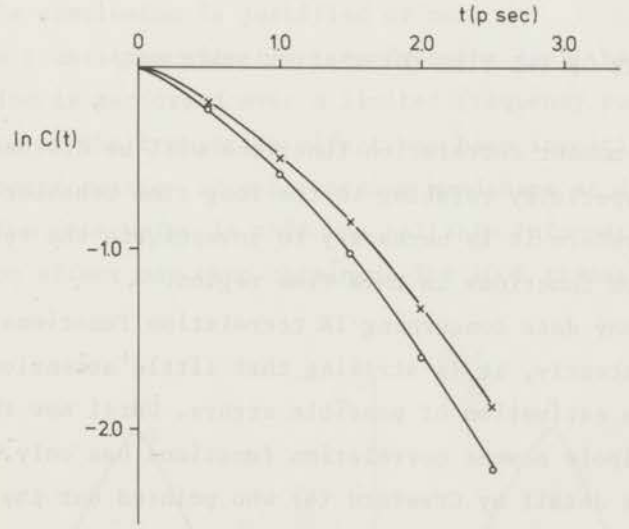

Fig.3. Ln C(t) for the absorption band of $CDCl_3$ at 910 cm^{-1}.
×: calculated with n(ω).
o: calculated without n(ω).

index. It has to be stressed that all other investigated systems behave like $CHCl_3$.

It is to be noted here that eqn.(2) is only correct if the width at half intensity $\Delta\omega_{\frac{1}{2}} << \omega_0$($\Delta\omega_{\frac{1}{2}}$ is determined by the frequencies at which $\alpha(\omega_i) = \frac{1}{2}\alpha(\omega_0)$) and if the absorption band is localized at sufficiently high frequency. If these conditions are not fulfilled it is necessary to calculate the cosine transform of $\mathrm{cotgh}(\frac{1}{2}\beta\hbar\omega)n(\omega)k(\omega)$.

Four absorption bands have been studied using the isotopic dilution method; the band of CH_2Cl_2 at 1265 cm^{-1} (in CD_2Cl_2), $CHCl_3$ at 1215 cm^{-1} (in $CDCl_3$), $CHBr_3$ at 1142 cm^{-1} (in $CDBr_3$) and $CDCl_3$ at 910 cm^{-1} (in $CHCl_3$). All systems have been investigated over an extended concentration range, at a temperature of 30°C. The bandshapes of CH_2Cl_2 and $CHCl_3$ have also been studied at various temperatures. For the bandshapes of $CHCl_3$, $CDCl_3$ and $CHBr_3$ dilution series in other solvents have also been performed to investigate the difference with isotopic dilution series. All chemicals used were obtained from E.Merck (Darmstadt) and were of spectroscopic grade.

2. THE RELIABILITY OF THE TIME CORRELATION FUNCTIONS

The dipole moment correlation functions will be discussed in the next chapters, especially relating to the long time behavior (1-3 psec.). Therefore it is necessary to investigate the reliability of the correlation functions in this time region.

Although many data concerning IR correlation functions have been published recently, it is striking that little attention has been given to the estimation of possible errors. Until now the reliability of dipole moment correlation functions has only been discussed in some detail by Crawford (4) who pointed out that errors may arise by several causes; the finite resolution of the spectrophotometer, the numerical procedure of integration, the truncation effect (dependent on the magnitude of the integration interval), the baseline effect (i.e. the 100% transmission line may be chosen wrongly) and random errors in the transmission values.

Because the spectral resolution was about 0.5 cm^{-1} the influence of the finite resolution is neglected here. This is justified by the

fact that a considerable improvement of the resolution by varying the slitwidth does not influence the bandshape. Errors due to the numerical procedure may also be ignored, because of the fact that the sampling density of transmission values is sufficiently high for each absorption band. This has been verified by varying the sampling density.

However, according to Crawford the truncation effect, the baseline effect and the random errors should give rise to dramatic deviations and oscillations of the time correlation functions. Especially at longer times (t>1 psec.) the correlation functions become increasingly inaccurate (the magnitude of the relative error in ln C(t) may be about 40% (5)). Therefore it is concluded that only the short time behavior gives reliable information on the investigated systems. This explains that several authors interpret only the short time behavior of the dipole moment correlation functions (4-11).

With respect to the present study, it is important to know if Crawford's conclusion is justified or not.

The truncation effect arises from the fact that the numerical calculation is performed over a limited frequency range. Therefore the importance of the truncation effect has been investigated by Fouriertransformation of a Lorentzian bandshape at different integration intervals. In this way reliable information over the truncation effect has been obtained. The 100% transmission line (or

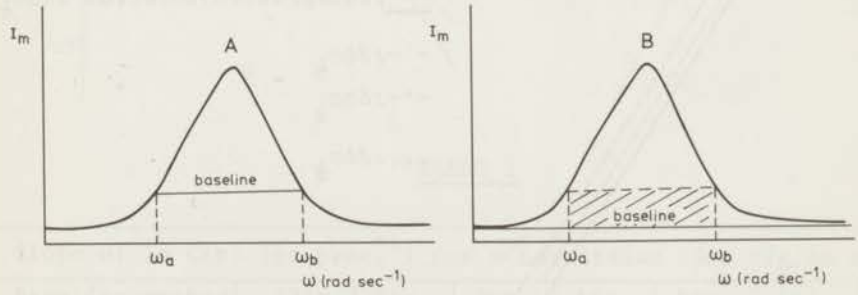

Fig.4. A: Baseline as used in the present study.
B: Baseline as used by Crawford (4).

baseline) is determined by the integration interval as pointed out in section 1. This means that the baseline is given by the line connecting the transmission values at the frequencies ω_a and ω_b. It should be noted that this procedure is different from the method used by Crawford (4). There, the baseline is independent on the integration interval. Variation of this range keeps the baseline at a fixed position, usually determined by transmission values as far as possible in the wings. This is illustrated in an exaggerated way by Fig.4, where for an arbitrary bandshape the baseline is indicated, using the method described in the previous section (Fig.4; A) and the method of Crawford (Fig.4; B).

The truncation effect on ln C(t) has been investigated for a Lorentzian bandshape (width at half intensity 14 cm^{-1}). It should be noted here that throughout this thesis the width at half intensity is usually expressed in cm^{-1} units. This is indicated by using the symbol $\Delta\sigma_{\frac{1}{2}}$ ($\Delta\sigma_{\frac{1}{2}}=2\pi c\Delta\omega_{\frac{1}{2}}$; c is the velocity of light). The frequency range has been taken respectively 13,8,7,6,5,4 and 3 times the width at half

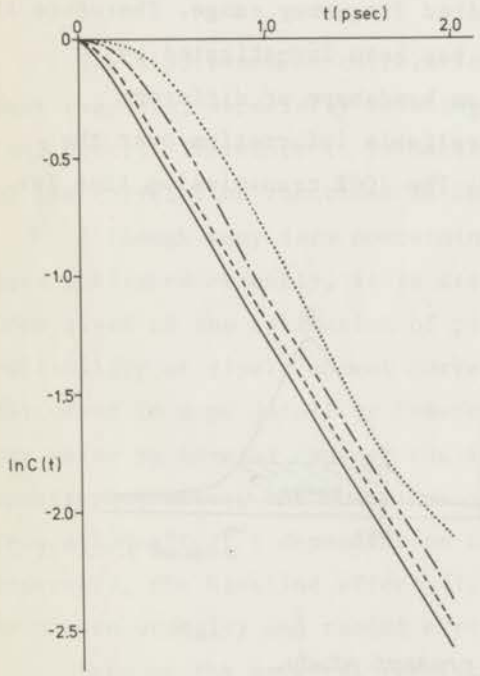

Fig.5a. Ln C(t) for a Lorentzian bandshape ($\Delta\sigma_{\frac{1}{2}}$=14 cm^{-1}) using baseline method A.

___:integration interval 13$\Delta\sigma_{\frac{1}{2}}$

- -:8$\Delta\sigma_{\frac{1}{2}}$

-·-:5$\Delta\sigma_{\frac{1}{2}}$

...:3$\Delta\sigma_{\frac{1}{2}}$

intensity. The results are shown in Fig.5a and Table I (method A). Apart from the deviations of the short time behavior of the correlation functions, the long time behavior is very insensitive to the narrowing of the frequency range. Although the value of ln C(t) changes systematically at longer times due to the narrowing of the integration interval, the slope of ln C(t) at longer times remains constant. The correlation functions are not oscillating, contrary to the results of Crawford (4). It seems sufficient to take a frequency range of about five times the width at half intensity of the absorption band.

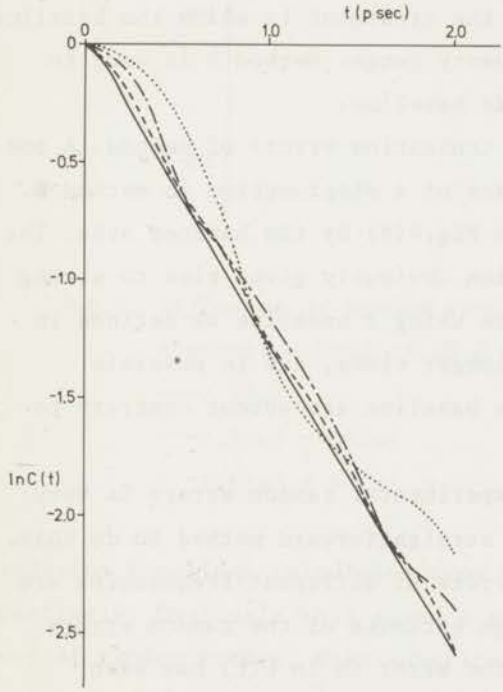

Fig.5b. Ln C(t) for a Lorentzian bandshape ($\Delta\sigma_{\frac{1}{2}}$=14 cm^{-1}) using baseline method B.

——: *integration interval* $13\Delta\sigma_{\frac{1}{2}}$

- -: $8\Delta\sigma_{\frac{1}{2}}$

-·-: $5\Delta\sigma_{\frac{1}{2}}$

...: $3\Delta\sigma_{\frac{1}{2}}$

TABLE I

Slope of ln C(t) (in $psec.^{-1}$) for a Lorentzian (See Fig.5a and 5b)							
Baseline method	$13\Delta\sigma_{\frac{1}{2}}$	$8\Delta\sigma_{\frac{1}{2}}$	$7\Delta\sigma_{\frac{1}{2}}$	$6\Delta\sigma_{\frac{1}{2}}$	$5\Delta\sigma_{\frac{1}{2}}$	$4\Delta\sigma_{\frac{1}{2}}$	$3\Delta\sigma_{\frac{1}{2}}$
A	-1.28	-1.28	-1.29	-1.28	-1.30	-1.24	-1.34
B	-1.28	-1.26	-1.27	-1.28	-1.30	-1.42	-0.79

The reason that the data given here do not confirm Crawford's results is due to the different choice of the baseline. Investigating the truncation effect using a fixed baseline (Fig.4;B) the time correlation functions show oscillations with the narrowing of the frequency range, like Crawford's data (4). This is shown in Fig.5b.

However, using baseline method B the slope of ln C(t) is reasonably accurate. The slope, determined from the long time behavior, corresponds reasonable well to the slope obtained from the other baseline method (Table I). In this context the slope has been defined as the slope of the straight line fitted to the oscillating function ln C(t) by a least squares procedure in the time interval 1-3 psec. In Table I method A is the treatment in which the baseline is changed on narrowing the frequency range. Method B is used to indicate the approach with a fixed baseline.

The difference between the truncation errors of method A and B (Fig.4) is caused by the presence of a stepfunction in method B. This stepfunction is indicated in Fig.4(B) by the hatched area. The cosine transform of such a function obviously gives rise to strong oscillations in ln C(t). Therefore using a baseline as defined in method A, the enormous error at longer times, due to possible deviations in the position of the baseline are absent contrary to method B (4).

The investigation of the experimental random errors is very complicated, because there is no straightforward method to do this. For example, it is unknown how errors at different frequencies are correlated. Therefore only a rough estimate of the random errors is possible. The calculation of the error in ln C(t) has been performed by Crawford by substituting in eqn.(2) the expected maximum deviation $\Delta k(\omega_i)$ of $k(\omega_i)$ for the extinction coefficient $\alpha(\omega_i)$. In this way the maximum error in the correlation function is obtained as a function of time. It is shown that after 0.5 psec. the time correlation function becomes very unreliable.

However, on the basis of the experimental reproducibility it may be expected that Crawford's considerations give an overestimation of the errors. This is underlined by comparing the dipole moment

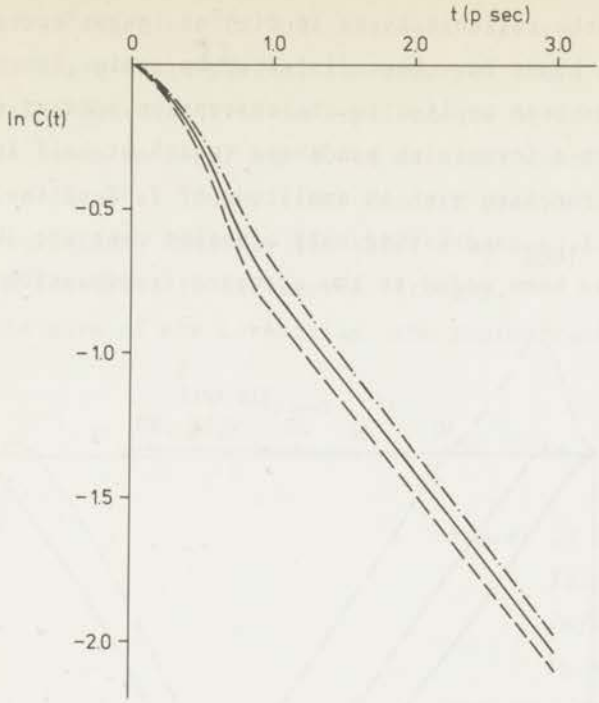

Fig.6. Influence of random errors on ln C(t) of the absorption band of CD_3J at 495 cm^{-1} (4).
——: $k(\omega)$
-·-: $k(\omega) - \Delta k(\omega)$
- -: $k(\omega) + \Delta k(\omega)$

correlation functions calculated from $k(\omega_i)$ and $k(\omega_i) \pm \Delta k(\omega_i)$ respectively. Obviously this gives a more realistic impression of the effect of random errors, than substituting $\Delta k(\omega_i)$ in eqn.(2). Treating in this way the values of $k(\omega_i)$ and $\Delta k(\omega_i)$ for CD_3J (absorption band at 495 cm^{-1}) presented by Crawford (4), it can be shown that the errors $\Delta k(\omega_i)$ only affect significantly the short time behavior. The slope at longer times remains unchanged (Fig.6). This result supports the impression already obtained from experimental reproducibility that contrary to Crawford's opinion the long time behavior of the correlation function is less sensitive to errors than the short time behavior.

To consider the reliability of ln C(t) at longer times in more detail, absorption bands have been distorted by cosine functions. This procedure has been applied to the absorption band of neat $CHCl_3$ at 1215 cm^{-1} and to a Lorentzian bandshape (width at half intensity 5 cm^{-1}). A cosine function with an amplitude of 2.5% of the difference between I_{zero} and $I_{100\%}$ and having half a period over the investigated frequency range has been added to the observed transmission spectra

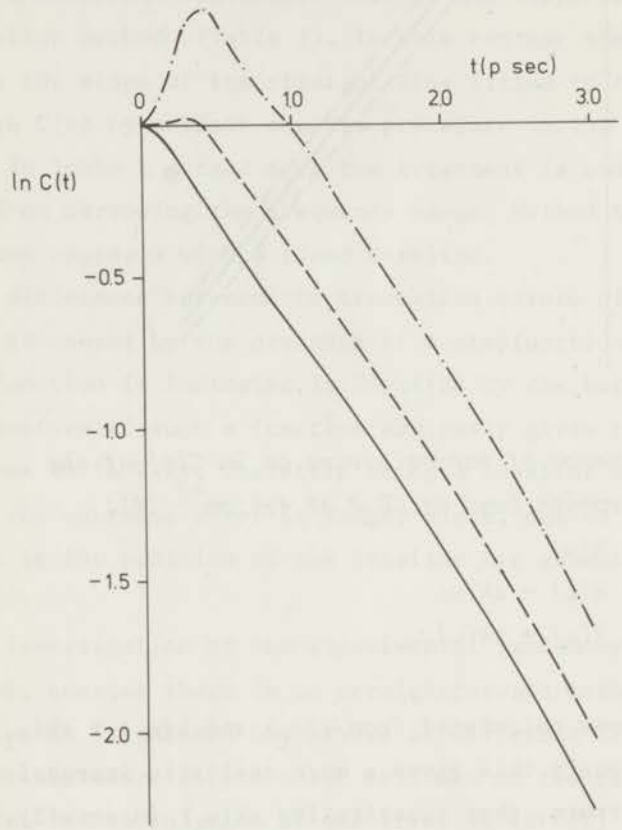

Fig.7. Ln C(t) of $CHCl_3$ at 1215 cm^{-1} (30°C). Influence of bandshape distortions by cosine functions.
– –: amplitude 2.5% of (I_{zero}-$I_{100\%}$); 1 period
–·–: amplitude 5.0%; 1 period
——: undistorted curve and the results of the distortions with cosine functions of half a period.

of $CHCl_3$ at 30°C and -60°C. This has been repeated with a cosine function having a whole period. The same procedure has been performed using a cosine function with an amplitude of 5% of ($I_{zero}-I_{100\%}$). The results are shown in Fig.7 and 8. It is clear from these figures that the relative decay at longer times (t> 0.5 psec.) is very insensitive to the perturbation. However, the short time behavior of the correlation functions is influenced strongly.

In the case of the Lorentzian the cosine functions have been

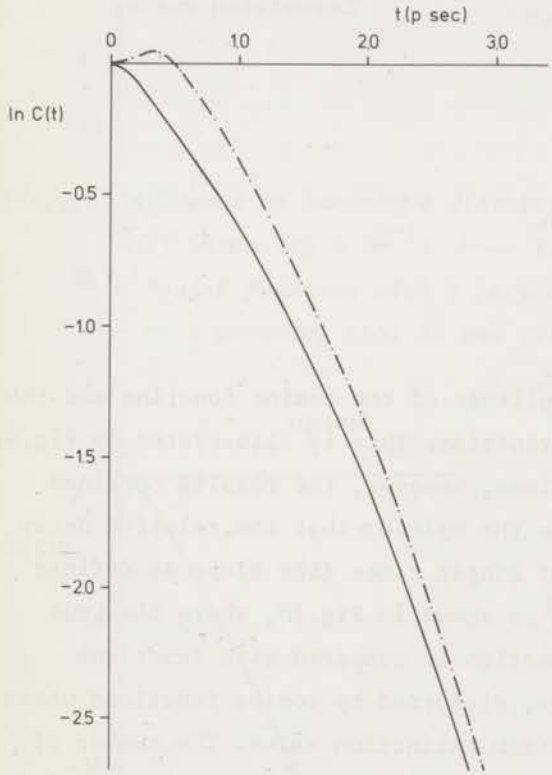

Fig.8. Ln C(t) of $CHCl_3$ at 1215 cm^{-1} (-60°C). Influence of distortions by cosine functions.
-·-:amplitude 5%; 1 period
——:undistorted curve
All other calculations performed did not show deviations from the undistorted curve.

added to the extinction curve rather than to the transmission curve (as was done in the case of $CHCl_3$). Therefore the numerical calculation procedure used for the Lorentzian curve, introduces oscillations due to the fact that the baseline is not determined by the extinction values at the boundaries of the integration interval. The cosine functions have been added to the Lorentzian in such a way that the boundaries of the frequency range investigated have an extinction

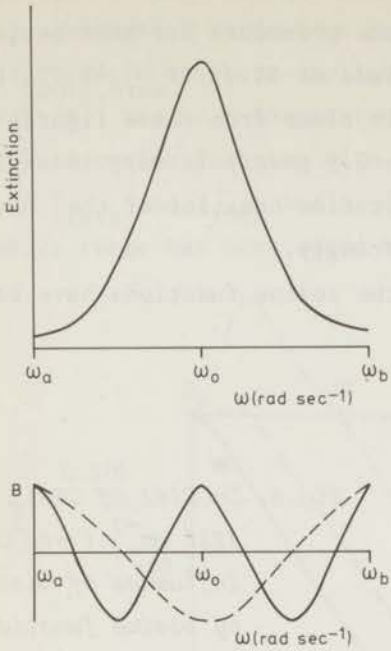

Fig.9. Illustration of the stepfunction introduced in the calculation of the influence of bandshape distortions on a Lorentzian curve.

value, being the sum of the amplitude of the cosine function and the extinction value due to the Lorentzian. This is illustrated by Fig.9. Irrespective of these oscillations, however, the results obtained from the calculations underline the opinion that the relative decay of the correlation functions at longer times (the slope as defined before) is very reliable. This is shown in Fig.10, where the true Lorentzian time correlation function is compared with functions obtained from extinction curves, distorted by cosine functions whose amplitudes are 2.5% of the maximum extinction value. The number of periods over the frequency range investigated is respectively 1,2,8, 32 and 128.

Another uncertainty concerning time correlation functions may arise from an inaccuracy in the determination of the zero transmission line. Investigating the influence of a change on I_{zero} of about 0.5% (which is a reasonable estimate for the experimental fluctuation) no effect on the time correlation function occurs. This is illustrated in Fig.11 for the absorption band of $CHBr_3$ at 1142 cm^{-1} (in $CDBr_3$,

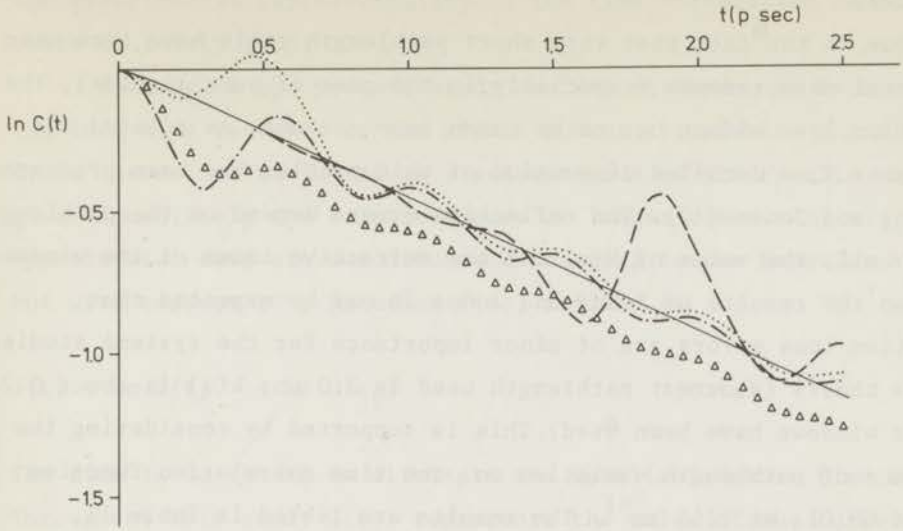

Fig. 10. Influence of bandshape distortion on a Lorentzian (width at half intensity 5 cm^{-1}). ——: true curve; -·-: distortion by a cosine function with 1 period; ...: 2 periods; - -: 8 periods; ΔΔΔ: 32 and 128 periods.

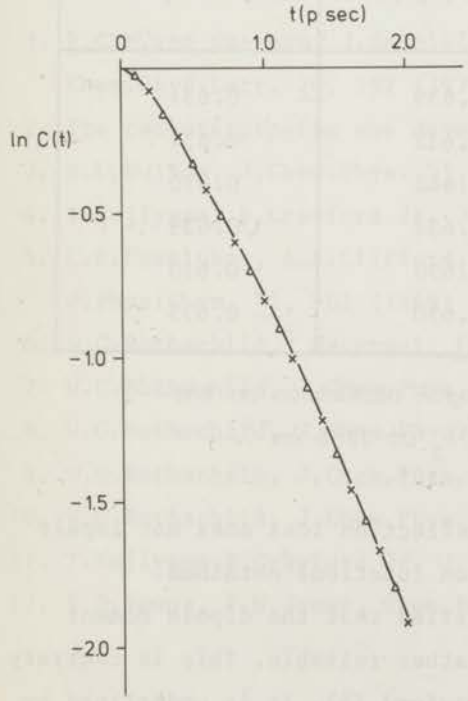

Fig. 11. Investigation of the effect of varying the zero transmission line for the absorption band of $CHBr_3$.
Δ: result when using I_{zero} measured
×: change of 0.5% on I_{zero} measured.

33 vol.%).

Due to the fact that very short pathlength cells have been used in several measurements (especially in the case of pure liquids), the reflection loss effect has to be taken into account. As pointed out in Chapter I, a detailed discussion of this problem has been presented by Young and Jones (12). The reflection errors depend on the pathlength of the cell, the value of $k(\omega)$ and the refractive index of the windows. Based on the results of Young and Jones it may be expected that reflection loss errors are of minor importance for the systems studied in this thesis (shortest pathlength used is 2.5 μm; $k(\omega)$ is about 0.2 and KBr windows have been used).This is supported by considering the influence of pathlength variation on the time correlation function of neat CH_2Cl_2 at 1265 cm^{-1}. The results are listed in Table II, where both $\Delta\sigma_{\frac{1}{2}}$ and $\left|\frac{\Delta(\ln C(t))}{\Delta t}\right|$ (from the slope of the time correlation function at longer times) remain fairly constant.

TABLE II

Pathlength (μm)	$\Delta\sigma_{\frac{1}{2}}$ (cm^{-1})	$\left\|\frac{\Delta(\ln C(t))}{\Delta t}\right\|$ ($psec^{-1}$)	
		From 1-2 psec.	From 1-3 psec.
6.4	6.9	0.639	0.631
5.3	7.0	0.632	0.631
3.9	7.1	0.665	0.670
2.8	7.1	0.634	0.639
1.7	7.2	0.690	0.610
1.0	7.1	0.650	0.635

Table II. Influence of pathlength variation on the IR bandshape of CH_2Cl_2 at 1265 cm^{-1}.

Therefore it may be concluded that reflection loss does not impair the reliability of the autocorrelation functions obtained.

Finally the conclusion is justified that the dipole moment correlation functions obtained are rather reliable. This is contrary to the widely accepted opinion of Crawford (4). It is underlined by

the experimental reproducibility of the time correlation functions, which is fairly good.

Because in the present study special attention is focused on the long time behavior of the dipole moment correlation functions it is convenient to introduce a presentation of the results which gives immediately the relative decay at longer times. Therefore the experimental data are not discussed relating to the behavior of ln C(t) but with respect to a function f(t), defined as

$$f(t) \equiv \ln C(t) - \ln C(t_0) \qquad (t \geqslant t_0) \qquad (3)$$

The time t_0 is chosen to eliminate the unreliable short time behavior. Throughout this study $C(t_0)$ represents the value of the correlation function at 1 psec. The behavior of f(t) after 1 psec. will be presented in the following chapters.

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CHAPTER III

EXPERIMENTAL RESULTS

In this chapter the experimental data are presented. The IR bandshapes have been recorded and transformed into time correlation functions according to the method described in Chapter II. The results of the isotopic dilution series are given in section 1 (measurements at a temperature of 30°C) and 2 (study of the influence of decreasing temperature). Section 3 deals with dilution series in various solvents (such as CCl_4, CS_2, etc.).

The investigation of the isotopic dilution effect at 30°C has been confined to four absorption bands; the 1265 cm^{-1} band of CH_2Cl_2, the 1215 cm^{-1} band of $CHCl_3$, the 910 cm^{-1} band of $CDCl_3$ and the band of $CHBr_3$ at 1142 cm^{-1}. The influence of the temperature has been studied for CH_2Cl_2 and $CHCl_3$, while for $CHCl_3$, $CDCl_3$ and $CHBr_3$ dilution series have been performed using several other solvents.

1. ISOTOPIC DILUTION SERIES AT 30°C

The absorption bands considered here all satisfy the condition that they have to be isolated from other absorptions in the spectrum (See Ch.II). Furthermore, the solvents used are transparent over a wide range in the frequency region of interest.

The variation of the refractive index $n(\omega)$ was taken into account in the calculation of the time correlation functions (1). However, as pointed out before, the refractive index has a negligible influence except in the case of $CDCl_3$ (See Ch.II; Fig.2 and 3).

TABLE I

Absorption band of CH_2Cl_2 at 1265 cm^{-1} (in CD_2Cl_2)

concentration		path	shift	B	$\Delta\sigma_{\frac{1}{2}}$	$\left\|\frac{\Delta f(t)}{\Delta t}\right\|$ ($psec^{-1}$)	
$mol.l.^{-1}$	molfr.	length(μm)	$\Delta\sigma(cm^{-1})$	$(l.mol.^{-1}cm^{-2})$	(cm^{-1})	1-2 ps.	2-3 ps.
15.77	1.0	2.5	0.0	1420	7.2	0.69	0.69
13.0	0.84	2.8	+0.2	1380	6.9	0.63	0.67
10.0	0.64	3.4	+0.3	1310	6.6	0.63	0.61
8.0	0.51	4.4	+0.2	1300	6.5	0.59	0.57
6.0	0.39	7.8	+0.4	1260	6.3	0.57	0.58
4.0	0.26	8.1	+0.4	1240	6.1	0.56	0.54
1.5	0.096	34.5	+0.5	1230	5.8	0.55	0.55

Absorption band of $CHCl_3$ at 1215 cm^{-1} (in $CDCl_3$)

concentration		path	shift	B	$\Delta\sigma_{\frac{1}{2}}$	$\left\|\frac{\Delta f(t)}{\Delta t}\right\|$ ($psec^{-1}$)	
$mol.l.^{-1}$	molfr.	length(μm)	$\Delta\sigma(cm^{-1})$	$(l.mol.^{-1}cm^{-2})$	(cm^{-1})	1-2 ps.	2-3 ps.
12.31	1.0	3.5	0.0	1600	8.2	0.75	0.86
10.0	0.82	7.8	+0.3	1530	7.7	0.70	0.77
8.0	0.65	8.1	+0.3	1380	7.4	0.68	0.73
4.0	0.32	8.1	+0.5	1530	7.2	0.63	0.68
1.0	0.082	34.5	+0.5	1390	6.4	0.60	0.61
0.5	0.041	80.4	+0.6	1480	6.4	0.57	0.62

Absorption band of $CDCl_3$ at 910 cm^{-1} (in $CHCl_3$)

concentration		path	shift	B	$\Delta\sigma_{\frac{1}{2}}$	$\left\|\frac{\Delta f(t)}{\Delta t}\right\|$ ($psec^{-1}$)	
$mol.l.^{-1}$	molfr.	length(μm)	$\Delta\sigma(cm^{-1})$	$(l.mol.^{-1}cm^{-2})$	(cm^{-1})	1-2 ps.	2-3 ps.
12.45	1.0	2.5	0.0	4790	14.5	1.30	1.81
5.0	0.41	4.2	0.0	4950	11.8	1.17	1.62
3.0	0.25	4.2	+0.4	5270	11.0	1.05	1.48
1.6	0.13	4.2	+0.2	4310	10.0	0.91	1.13
0.60	0.050	33.1	+0.1	4880	9.8	0.88	1.02
0.30	0.025	90.4	0.0	5030	9.8	0.93	1.12

Absorption band of $CHBr_3$ at 1142 cm^{-1} (in $CDBr_3$)

concentration		path	shift	B	$\Delta\sigma_{\frac{1}{2}}$	$\left\|\frac{\Delta f(t)}{\Delta t}\right\|$ ($psec^{-1}$)
$mol.l.^{-1}$	molfr.	length(μm)	$\Delta\sigma(cm^{-1})$	$(l.mol.^{-1}cm^{-2})$	(cm^{-1})	1-2 ps.
11.40	1.0	5.4	0.0	2700	12.8	1.30
8.55	0.75	5.7	+0.5	2589	12.3	1.26
5.70	0.50	9.9	+1.0	2276	11.6	1.15
3.80	0.33	9.9	+1.3	2341	11.3	1.12
2.31	0.20	10.2	+1.5	2435	11.0	1.08
0.569	0.05	90.4	+1.9	2546	10.2	1.02

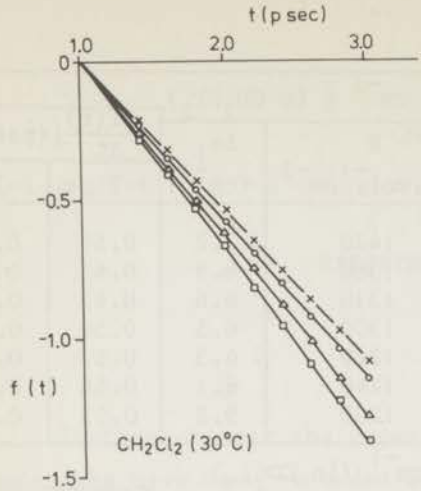

Fig.1. CH_2Cl_2 *in* CD_2Cl_2.
□: *molfr. 1.0* Δ: *0.84*
o: *0.39* ×: *0.0*

The results are presented in detail in Table I and Fig.1-4. Table I gives for each solution measured the main parameters, characterising the corresponding absorption band and dipole moment correlation function; the width at half intensity of the absorption band $\Delta\sigma_{\frac{1}{2}}$, the frequency shift $\Delta\sigma$ with respect to the frequency σ_0 of the absorption band maximum of the pure liquid, the path length of the cell used in the experiment, the concentration in mol.l.$^{-1}$ and expressed in molefractions, the integrated absorption intensity B (in

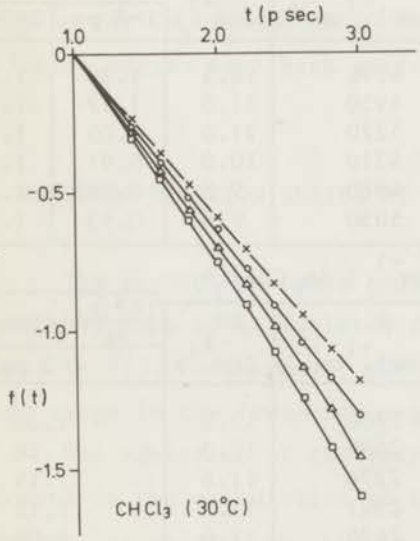

Fig.2. $CHCl_3$ *in* $CDCl_3$.
□: *molfr. 1.0* Δ: *0.82*
o: *0.32* ×: *0.0*

$l.mol.^{-1}cm^{-2}$) and $|\frac{\Delta f(t)}{\Delta t}|$ (in $psec^{-1}$) which is a measure for the decay of f(t) (as defined in Ch.II; eqn.(3)). In the table two values of $|\frac{\Delta f(t)}{\Delta t}|$ have been listed determined from two different time intervals of the correlation function (From 1-2 psec. and 2-3 psec. respectively; with exception of $CHBr_3$ because in this case only data till 2 psec. have been obtained).

Especially when the time correlation functions correspond well to exponential functions (i.e. the absorption band has a Lorentzian shape) the change of $|\frac{\Delta f(t)}{\Delta t}|$ on isotopic dilution gives a good estimate of the effect of the intermolecular vibrational relaxation

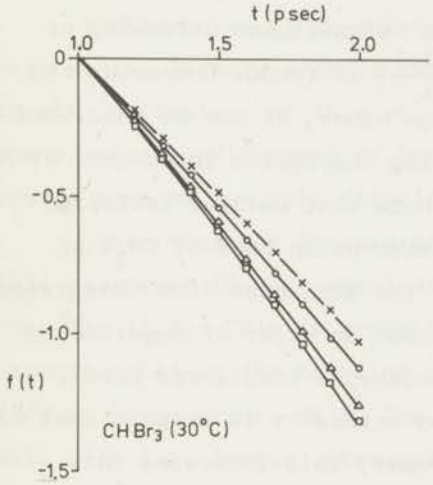

Fig.3. $CHBr_3$ in $CDBr_3$.
□: molfr. 1.0 Δ: 0.75
o: 0.33 ×: 0.0

on the bandshape. In these cases $\Delta\sigma_{\frac{1}{2}}$ is directly related to $|\frac{\Delta f(t)}{\Delta t}|$ as is well known ($|\frac{\Delta f(t)}{\Delta t}|=\pi c\Delta\sigma_{\frac{1}{2}}$) and may equally well be used to discuss the influence of the interoscillator coupling. However, the presented values for $|\frac{\Delta f(t)}{\Delta t}|$ show that an exponential decay for the correlation function is not generally found. This is demonstrated by Fig.1-4, although it may be concluded that especially for CH_2Cl_2 an exponential decay is a reasonable approximation. In section 2 the results at low temperatures will show much larger deviations from an exponential behavior. In these cases a simple relation between $\Delta\sigma_{\frac{1}{2}}$ and f(t) fails; the change of $\Delta\sigma_{\frac{1}{2}}$ on isotopic dilution will only be a

rough estimate of the effect on the bandshape. To obtain detailed information about the isotopic dilution effect on IR bandshapes it is preferable to consider f(t) as displayed in Fig.1-4.

For the four investigated absorption bands f(t) is shown for several concentrations and the infinite isotopic dilution. The infinite dilution curve ($f_0(t)$ in the following) has been obtained by an extrapolation of f(t) to concentration zero.

It is clear from the listed data in Table I and the curves in Fig.1-4 that all the investigated absorption bands show a significant isotopic dilution effect. Considering $|f(t)|$ it can immediately be shown that $|f(t)|$ decreases gradually with decreasing concentration for each absorption band. Furthermore a significant narrowing of $\Delta\sigma_{\frac{1}{2}}$ and a corresponding decrease of $\left|\frac{\Delta f(t)}{\Delta t}\right|$ is found. Comparing the measured effects for the four absorption bands, it may be concluded that the effect increases with increasing absorption intensity. With respect to this, it is interesting to note that earlier isotopic dilution measurements (2) of the weak absorption band of CH_3J at 522 cm^{-1} did not show any narrowing of the bandshape (the integrated absorption intensity of this band is about an order of magnitude smaller than the intensities of the bandshapes considered here).

Because the integrated absorption intensity is proportional to the square of the transition dipole moment, this indicates that

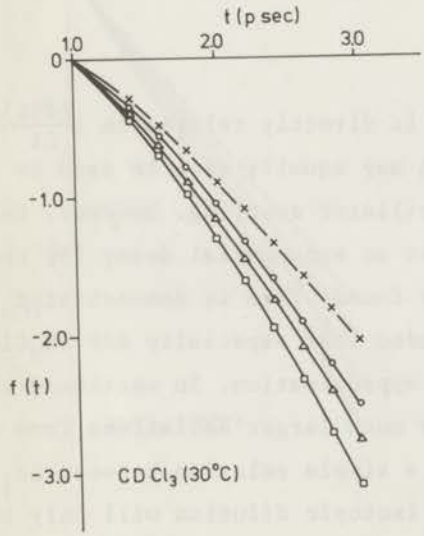

Fig.4. $CDCl_3$ in $CHCl_3$.
□: molfr. 1.0 Δ: 0.41
o: 0.25 ×: 0.0

transition dipole-transition dipole interaction may be involved. With respect to this it is important to remark that dilution series often show an intensity dependent effect on $\Delta\sigma_{\frac{1}{2}}$ (3-5). Relating to this, several theoretical calculations have been performed to estimate the contribution of the transition dipole-transition dipole coupling to the halfwidth (3,5,6).

In Chapter IV the contribution of the transition dipole-transition dipole coupling to the intermolecular vibrational relaxation is estimated theoretically. It should be noted here that the theoretical expression, which will be derived in the next chapter can be compared directly with $f(t)-f_0(t)$.

Furthermore, it is interesting that the frequency shift $\Delta\sigma$ is very small. Because a shift can be interpreted in terms of a change in the intermolecular interactions (7) this supports the opinion that the physical environment of the investigated molecules does not change much on isotopic dilution.

Concerning the integrated intensity B it is to be noted that this parameter is very unreliable, contrary to the function f(t) (See Ch. II.2). This is probably due to the fact that small uncertainties in the baseline and the 100% transmission line give rise to large errors in B. The magnitude of the values obtained agrees well with data in the literature (Table II).

TABLE II

	$B(l.mol.^{-1}cm^{-2})$	Literature values
CH_2Cl_2	1420	1174 (8)
$CHCl_3$	1600	1261 (9)
		1660 (10)
$CHBr_3$	2700	2448 (10)
$CDCl_3$	4790	5826 (11)
		5156 (10)

2. ISOTOPIC DILUTION SERIES AT VARYING TEMPERATURES

As pointed out in the preceding section, the intermolecular transition dipole-transition dipole interaction may contribute to the isotopic dilution effect. This type of interaction depends on the relative orientation of the interacting molecules. Therefore it is interesting to study the effect of a varying rate of reorientation of the interacting molecules on the isotopic dilution effect. This may be performed by repeating the experiments given in section 1 at varying temperatures. Obviously lowering of the temperature will decrease the rate of reorientation.

The absorption bands of CH_2Cl_2 (1265 cm^{-1}) and $CHCl_3$ (1215 cm^{-1}) have been investigated. CH_2Cl_2 has been studied between 30°C and -90°C; $CHCl_3$ between 30°C and -60°C. The results of these experiments are presented for each temperature in the same way as the presentation of the results in section 1 (See Table III (CH_2Cl_2), Table IV ($CHCl_3$),

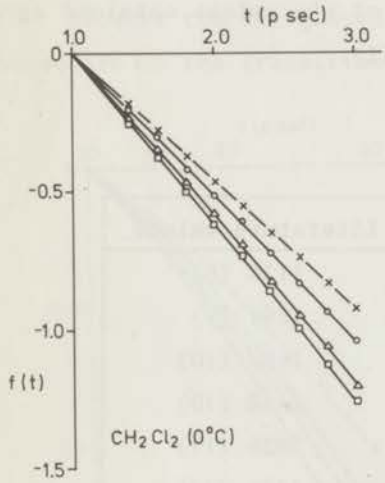

Fig.5. CH_2Cl_2 in CD_2Cl_2 (0°C).
□: molfr. 1.0 Δ: 0.84
o: 0.39 ×: 0.0

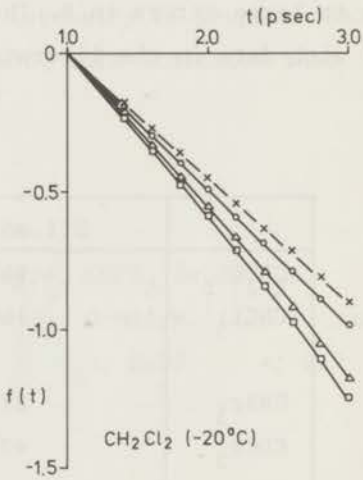

Fig.6. CH_2Cl_2 in CD_2Cl_2 (-20°C).
□: molfr. 1.0 Δ: 0.84
o: 0.39 ×: 0.0

Fig.5-10 (CH_2Cl_2) and Fig.11-14 ($CHCl_3$)).

TABLE III

CH_2Cl_2 (1265 cm^{-1}) at 0^oC						
concentration molfr.	path length(μm)	shift $\Delta\sigma(cm^{-1})$	B ($l.mol.^{-1}cm^{-2}$)	$\Delta\sigma_{\frac{1}{2}}$ (cm^{-1})	$\left\lvert\frac{\Delta f(t)}{\Delta t}\right\rvert$ ($psec^{-1}$) 1-2 ps.	2-3 ps.
1.0	2.5	0.0	1470	6.8	0.62	0.66
0.84	2.8	0.0	1490	6.5	0.57	0.62
0.64	3.4	+0.2	1300	6.3	0.57	0.56
0.51	4.4	+0.1	1310	6.3	0.55	0.59
0.39	7.8	+0.4	1320	5.7	0.51	0.54
0.26	8.1	+0.4	1390	5.7	0.51	0.49
CH_2Cl_2 (1265 cm^{-1}) at -20^oC						
concentration molfr.	path length(μm)	shift $\Delta\sigma(cm^{-1})$	B ($l.mol.^{-1}cm^{-2}$)	$\Delta\sigma_{\frac{1}{2}}$ (cm^{-1})	$\left\lvert\frac{\Delta f(t)}{\Delta t}\right\rvert$ ($psec^{-1}$) 1-2 ps.	2-3 ps.
1.0	2.5	0.0	1420	6.8	0.59	0.67
0.84	2.8	0.0	1560	6.4	0.56	0.62
0.64	3.4	+0.3	1310	6.2	0.54	0.55
0.51	4.4	+0.2	1460	6.1	0.56	0.56
0.39	7.8	+0.6	1330	5.3	0.49	0.51
0.26	8.1	+0.5	1380	5.3	0.48	0.50
CH_2Cl_2 (1265 cm^{-1}) at -40^oC						
concentration molfr.	path length(μm)	shift $\Delta\sigma(cm^{-1})$	B ($l.mol.^{-1}cm^{-2}$)	$\Delta\sigma_{\frac{1}{2}}$ (cm^{-1})	$\left\lvert\frac{\Delta f(t)}{\Delta t}\right\rvert$ ($psec^{-1}$) 1-2 ps.	2-3 ps.
1.0	2.5	0.0	1460	6.9	0.58	0.70
0.84	2.8	0.0	1610	6.6	0.56	0.63
0.64	3.4	+0.2	1360	6.4	0.56	0.62
0.51	4.4	+0.2	1470	6.2	0.56	0.57
0.39	7.8	+0.5	1410	5.5	0.46	0.53
0.26	8.1	+0.3	1410	5.4	0.46	0.49
0.096	34.5	+0.5	1340	4.8	0.44	0.44
CH_2Cl_2 (1265 cm^{-1}) at -60^oC						
concentration molfr.	path length(μm)	shift $\Delta\sigma(cm^{-1})$	B ($l.mol.^{-1}cm^{-2}$)	$\Delta\sigma_{\frac{1}{2}}$ (cm^{-1})	$\left\lvert\frac{\Delta f(t)}{\Delta t}\right\rvert$ ($psec^{-1}$) 1-2 ps.	2-3 ps.
1.0	2.5	0.0	1590	7.2	0.62	0.73
0.84	2.8	0.0	1600	6.9	0.58	0.69
0.64	3.4	+0.2	1530	6.8	0.58	0.67

(continued on page 48)

TABLE III (continuation)

0.51	4.4	+0.2	1490	6.5	0.56	0.61
0.39	7.8	+0.6	1450	5.8	0.48	0.55
0.26	8.1	+0.4	1410	5.8	0.46	0.51

CH_2Cl_2 (1265 cm^{-1}) at -75°C

concentration molfr.	path length(μm)	shift $\Delta\sigma(cm^{-1})$	B $(l.mol.^{-1}cm^{-2})$	$\Delta\sigma_{\frac{1}{2}}$ (cm^{-1})	$\lvert\frac{\Delta f(t)}{\Delta t}\rvert$ $(ps.^{-1})$ 1-2 ps.	2-3 ps.
1.0	2.5	-0.2	1700	8.2	0.68	0.88
0.84	2.8	-0.2	1630	7.7	0.63	0.85
0.64	3.4	+0.2	1490	7.2	0.57	0.70
0.51	4.4	+0.1	1590	7.1	0.59	0.70
0.39	7.8	+0.4	1470	6.3	0.51	0.61
0.26	8.1	+0.5	1370	6.0	0.48	0.56

CH_2Cl_2 (1265 cm^{-1}) at -90°C

concentration molfr.	path length(μm)	shift $\Delta\sigma(cm^{-1})$	B $(l.mol.^{-1}cm^{-2})$	$\Delta\sigma_{\frac{1}{2}}$ (cm^{-1})	$\lvert\frac{\Delta f(t)}{\Delta t}\rvert$ $(ps.^{-1})$ 1-2 ps	2-3 ps.
1.0	2.5	-0.4	1660	8.9	0.74	1.05
0.84	2.8	-0.3	1720	8.6	0.69	0.97
0.64	3.4	0.0	1540	7.9	0.63	0.83
0.51	4.4	+0.2	1600	7.8	0.63	0.83
0.39	7.8	+0.4	1480	6.8	0.53	0.68
0.26	8.1	+0.3	1420	6.7	0.52	0.65
0.096	34.5	+0.4	1270	6.2	0.48	0.56

Using the presented results interesting conclusions can be drawn. From Fig.5-14 it is clear that $|f(t)-f_0(t)|$ increases for each concentration with decreasing temperature. It is shown that the influence of the temperature becomes more important at longer times. Furthermore both for CH_2Cl_2 and $CHCl_3$ the narrowing of $\Delta\sigma_{\frac{1}{2}}$ with isotopic dilution increases on decreasing the temperature. As described in the previous section, CH_2Cl_2 shows a narrowing of 1.4 cm^{-1} (difference between the widths at half intensity of the pure liquid and the solution with concentration 1.5 $mol.l.^{-1}$) at 30°C. Decreasing the temperature to -90°C, this narrowing becomes 2.7 cm^{-1}. For $CHCl_3$ the narrowing at 30°C is 1.8 cm^{-1} (between neat liquid and the solution of 0.5 $mol.l.^{-1}$) while at -60°C it is 3.1 cm^{-1}. The changes of $|\frac{\Delta f(t)}{\Delta t}|$ on the temperature decrease behave roughly in the same way.

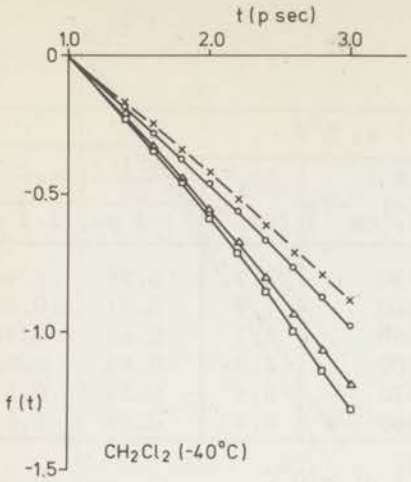

Fig. 7. CH_2Cl_2 *in* CD_2Cl_2 *(−40°C).*
□: *molfr. 1.0* Δ: *0.84*
o: *0.39* ×: *0.0*

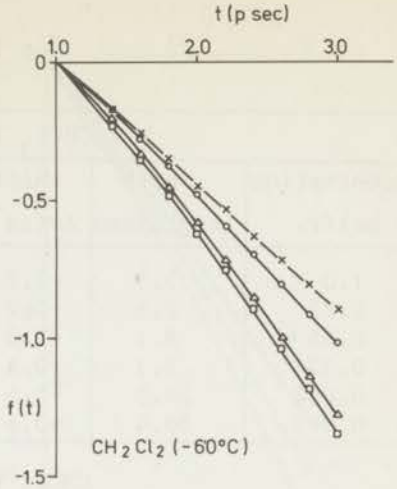

Fig. 8. CH_2Cl_2 *in* CD_2Cl_2 *(−60°C).*
□: *molfr. 1.0* Δ: *0.84*
o: *0.39* ×: *0.0*

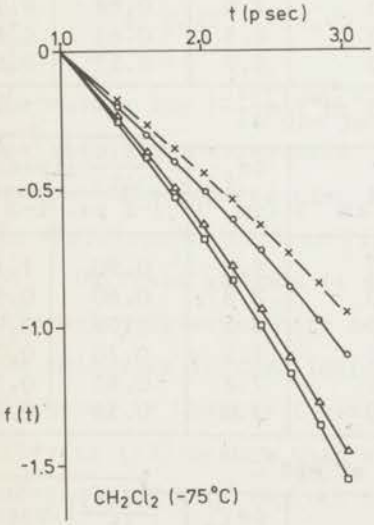

Fig. 9. CH_2Cl_2 *in* CD_2Cl_2 *(−75°C).*
□: *molfr. 1.0* Δ: *0.84*
o: *0.39* ×: *0.0*

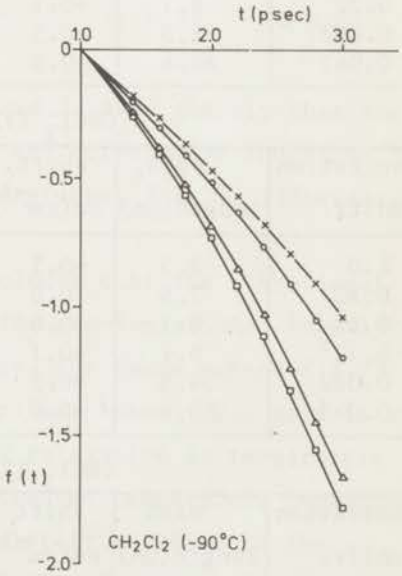

Fig. 10. CH_2Cl_2 *in* CD_2Cl_2 *(−90°C).*
□: *molfr. 1.0* Δ: *0.84*
o: *0.39* ×: *0.0*

TABLE IV

$CHCl_3$ (1215 cm^{-1}) at 0^oC						
concentration molfr.	path length(μm)	shift $\Delta\sigma(cm^{-1})$	B $(l.mol.^{-1}cm^{-2})$	$\Delta\sigma_{\frac{1}{2}}$ (cm^{-1})	$\lvert\frac{\Delta f(t)}{\Delta t}\rvert$ $(psec^{-1})$ 1-2 ps.	2-3 ps.
1.0	3.5	-0.2	1730	8.7	0.79	0.90
0.82	7.8	+0.2	1540	7.9	0.71	0.81
0.65	8.1	+0.2	1460	7.7	0.69	0.76
0.32	8.1	+0.4	1500	7.3	0.63	0.62
0.082	34.5	+0.5	1570	6.4	0.59	0.62
0.041	80.4	+0.6	1560	6.4	0.56	0.61
$CHCl_3$ (1215 cm^{-1}) at -20^oC						
concentration molfr.	path length(μm)	shift $\Delta\sigma(cm^{-1})$	B $(l.mol.^{-1}cm^{-2})$	$\Delta\sigma_{\frac{1}{2}}$ (cm^{-1})	$\lvert\frac{\Delta f(t)}{\Delta t}\rvert$ $(psec^{-1})$ 1-2 ps.	2-3 ps.
1.0	3.5	-0.4	1770	9.2	0.82	0.98
0.82	7.8	0.0	1620	8.4	0.75	0.87
0.65	8.1	+0.2	1470	7.9	0.71	0.81
0.32	8.1	+0.1	1510	7.6	0.68	0.76
0.082	34.5	+0.5	1430	6.8	0.61	0.66
0.041	80.4	+0.6	1650	6.7	0.57	0.64
$CHCl_3$ (1215 cm^{-1}) at -40^oC						
concentration molfr.	path length(μm)	shift $\Delta\sigma(cm^{-1})$	B $(l.mol.^{-1}cm^{-2})$	$\Delta\sigma_{\frac{1}{2}}$ (cm^{-1})	$\lvert\frac{\Delta f(t)}{\Delta t}\rvert$ $(psec^{-1})$ 1-2 ps.	2-3 ps.
1.0	3.5	-0.5	1800	9.8	0.90	1.16
0.82	7.8	0.0	1610	8.8	0.80	0.98
0.65	8.1	0.0	1520	8.5	0.75	0.92
0.32	8.1	+0.1	1520	7.9	0.70	0.79
0.082	34.5	+0.5	1450	7.2	0.63	0.74
0.041	80.4	+0.6	1580	7.0	0.58	0.69
$CHCl_3$ (1215 cm^{-1}) at -60^oC						
concentration molfr.	path length(μm)	shift $\Delta\sigma(cm^{-1})$	B $(l.mol.^{-1}cm^{-2})$	$\Delta\sigma_{\frac{1}{2}}$ (cm^{-1})	$\lvert\frac{\Delta f(t)}{\Delta t}\rvert$ $(psec^{-1})$ 1-2 ps.	2-3 ps.
1.0	3.5	-0.5	1800	10.6	0.99	1.44
0.82	7.8	-0.2	1650	9.7	0.90	1.19
0.65	8.1	0.0	1490	9.2	0.82	1.08
0.32	8.1	+0.1	1500	8.8	0.74	0.88
0.082	34.5	+0.4	1400	7.9	0.67	0.85
0.041	80.4	+0.6	1580	7.5	0.61	0.78

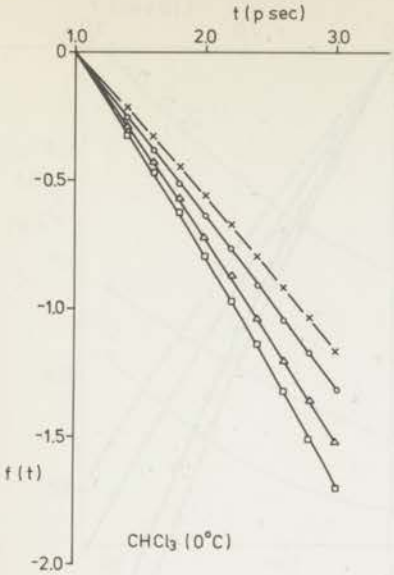

Fig.11. $CHCl_3$ in $CDCl_3$ (0^oC).
□: molfr. 1.0 Δ: 0.82
o: 0.32 ×:0.0

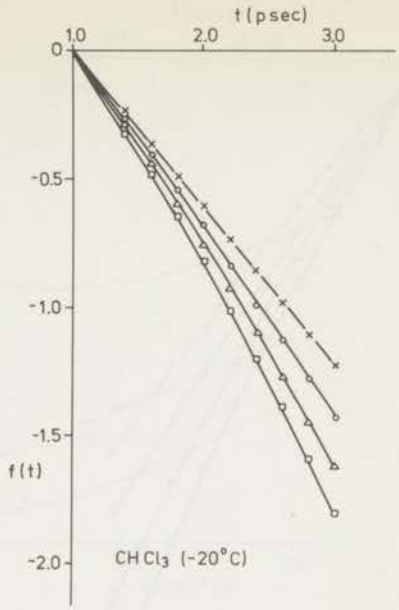

Fig.12. $CHCl_3$ in $CDCl_3$ (-20^oC).
□: molfr. 1.0 Δ:0.82
o: 0.32 ×:0.0

The values for $|\frac{\Delta f(t)}{\Delta t}|$ in Table III and IV show clearly that the deviation from exponential decay for the correlation functions becomes increasingly important at lower temperatures. This is illustrated in the plots of f(t) in Fig.5-14.

On these grounds it may be concluded that the vibrational relaxation observed here depends on the reorientational behavior of the molecules in the liquid. Therefore, the Rakov method (12,13) discussed in Chapter I can not be applied. Rakov (12), Bartoli and Litovitz (13) assume that vibrational relaxation is temperature independent. This implies that the observed temperature dependence of a correlation function can be completely ascribed to the reorientational correlation function. If this method is correct $\Delta\sigma_{\frac{1}{2}}$ and $|f(t)|$ will always decrease with decreasing temperature. The temperature dependence of the isotopic dilution effect directly shows that the basic assumption of the Rakov method (the vibrational relaxation is assumed to be temperature independent) is incorrect.

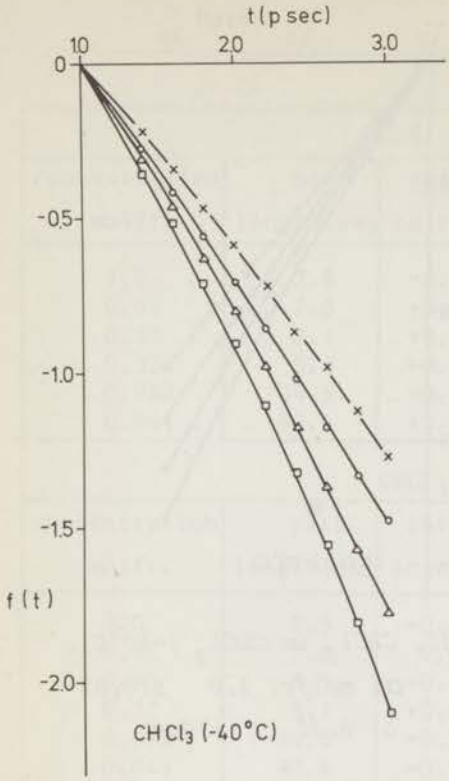

Fig.13. $CHCl_3$ in $CDCl_3$ (-40°C).
□: molfr. 1.0 Δ: 0.82
o: 0.32 ×: 0.0

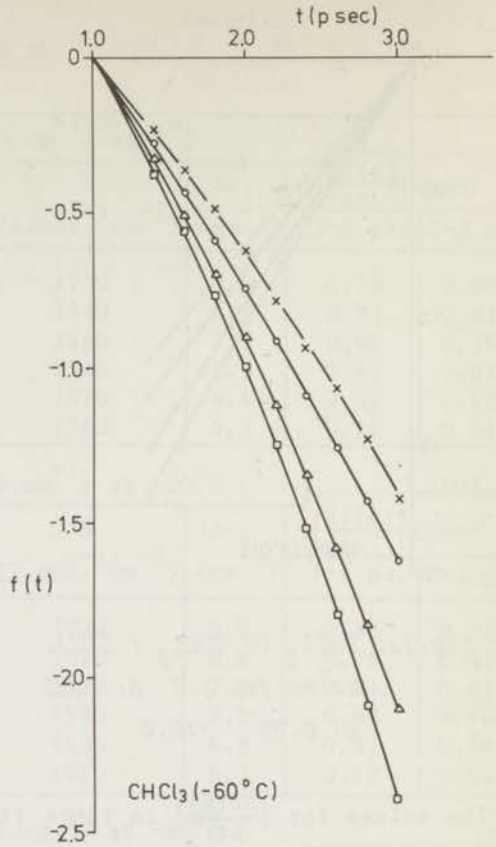

Fig.14. $CHCl_3$ in $CDCl_3$ (-60°C).
□: molfr. 1.0 Δ: 0.82
o: 0.32 ×: 0.0

This may imply that the widely used method (13,14) to separate the dipole moment correlation function into independent rotational and vibrational parts is incorrect, too.

It should be stressed that the temperature dependence of vibrational relaxation is not only due to the intermolecular vibrational relaxation, as determined by the isotopic dilution method. The experimental data clearly show that isotopically diluted solutions exhibit a temperature dependence, which is contrary to the assumptions underlying the Rakov method. This is illustrated by Fig.15-18, where for several concentrations the temperature dependence of $\Delta\sigma_{\frac{1}{2}}$ and $|f(3)|$ (value of $|f(t)|$ at t=3 psec.) is shown, both for

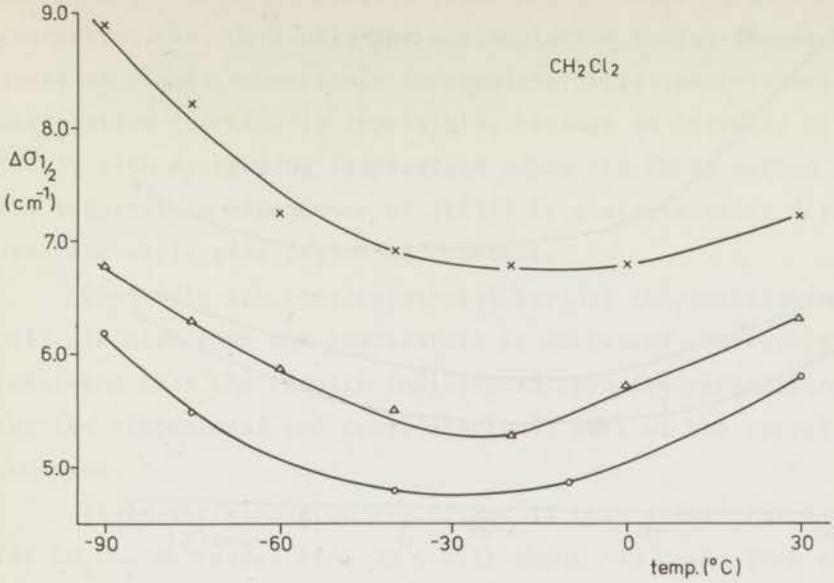

Fig. 15. The temperature dependence of $\Delta\sigma_{\frac{1}{2}}$ for CH_2Cl_2 at several concentrations. ×: molfr. 1.0 Δ: 0.39 o: 0.10

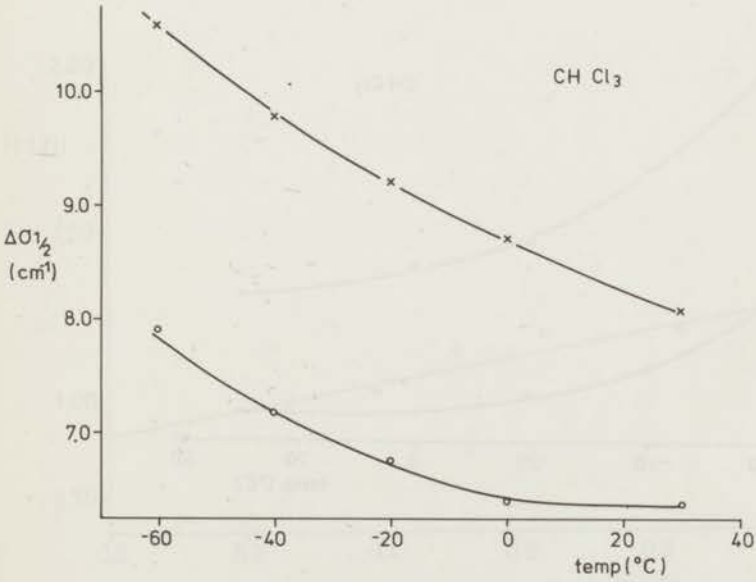

Fig. 16. The temperature dependence of $\Delta\sigma_{\frac{1}{2}}$ for $CHCl_3$ at several concentrations. ×: molfr. 1.0 o: 0.08

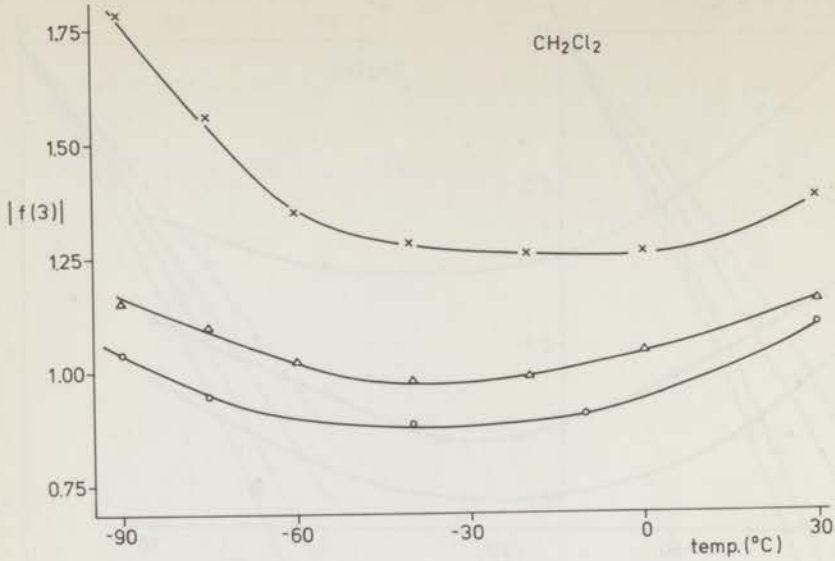

Fig. 17. The temperature dependence of $|f(3)|$ for CH_2Cl_2 at different concentrations. ×: molfr. 1.0 Δ: 0.39 o: 0.10

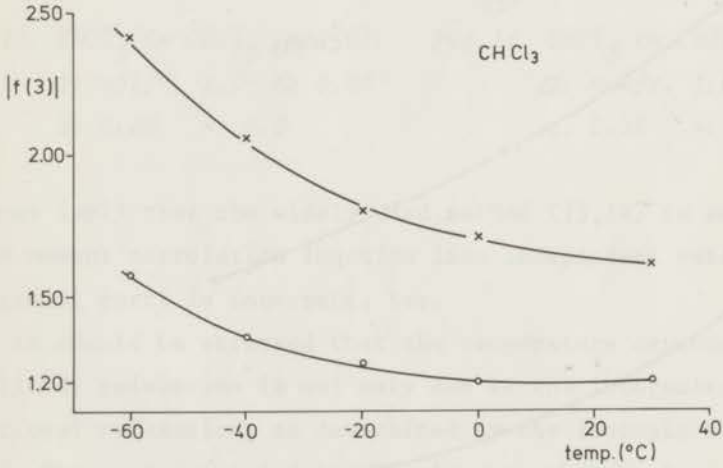

Fig.18. The temperature dependence of $|f(3)|$ for $CHCl_3$ at different concentrations. ×: molfr. 1.0 o: 0.08

CH_2Cl_2 and $CHCl_3$. The observed behavior is characteristic for all concentrations. Obviously the extrapolation to low temperature in order to find a temperature independent vibrational linewidth or correlation function is impossible, because an increase of $\Delta\sigma_{\frac{1}{2}}$ and $|f(t)|$ with decreasing temperature makes the Rakov method unuseful. The temperature dependence of $|f(3)|$ is characteristic for $|f(t)|$ over the whole time region of interest.

Obviously the reorientational part of the correlation function will diminish when the temperature is decreased. Therefore it may be concluded that the results indicate an opposite temperature dependence for the vibrational and reorientational part of the correlation function.

It is striking from Fig.17 and 18 that $|f(t)|$ (as $\Delta\sigma_{\frac{1}{2}}$; Fig.15,16) for CH_2Cl_2 decreases from 30°C till about -30°C and then starts to increase, while for $CHCl_3$ these parameters show a gradual increase over the whole investigated temperature range. Probably this must be ascribed to the fact that the reorientational contribution to the correlation function is more important for CH_2Cl_2. This can be

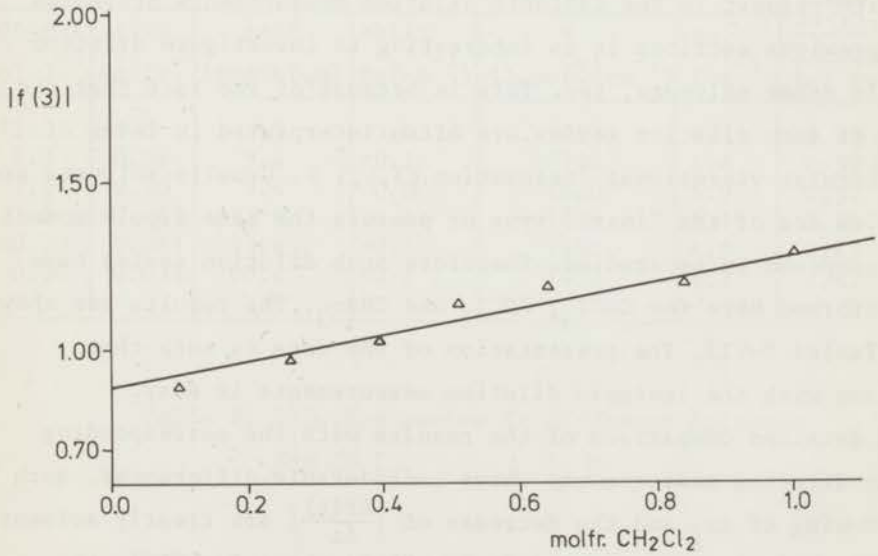

Fig. 19. Concentration dependence of $|f(3)|$ for CH_2Cl_2 at -40°C.

illustrated using NMR results (15,16). From these data it is known that the rotational correlation time τ_2 of CH_2Cl_2 (15) is considerably shorter than the one for $CHCl_3$ (16). Therefore it may be expected that the reorientational part of $|f(t)|$ for CH_2Cl_2 is larger than for $CHCl_3$. Taking into account that $|f(t)|$ for $CHCl_3$ exceeds the $|f(t)|$ value for CH_2Cl_2, it is clear that in the case of CH_2Cl_2 the reorientational part is more important than for $CHCl_3$.

Finally it is interesting to investigate the dependence of $|f(t)|$ on the concentration. Taking into account the experimental errors, it is concluded that a linear dependence of $|f(t)|$ on the concentration is most probable, although the experiments are not conclusive. In the next chapter it will be pointed out that a linear dependence is expected on theoretical grounds. An illustration of the change of $|f(t)|$ on dilution is given in Fig.19 for CH_2Cl_2 at an arbitrarily chosen temperature ($|f(3)|$is considered).

3. DILUTION SERIES IN DIFFERENT SOLVENTS AT 30°C

With respect to the isotopic dilution measurements presented in the previous sections it is interesting to investigate dilution series in other solvents, too. This is because of the fact that the results of such dilution series are often interpreted in terms of intermolecular vibrational relaxation (3,4,5). Usually solvents are used which are of the "inert" type or possess the same dipole moment as the compound to be studied. Therefore such dilution series have been performed here for $CHCl_3$, $CDCl_3$ and $CHBr_3$. The results are shown in the Tables V-VII. The presentation of the data is such that comparison with the isotopic dilution measurements is easy.

A detailed comparison of the results with the corresponding isotopic dilution measurements shows considerable differences. Both $\Delta\sigma$, the narrowing of $\Delta\sigma_{\frac{1}{2}}$ and the decrease of $|\frac{\Delta f(t)}{\Delta t}|$ are clearly solvent dependent. This is demonstrated in Fig.20-21 where for $CDCl_3$ the concentration dependence of $\Delta\sigma_{\frac{1}{2}}$ and $\Delta\sigma$ in several solvents (including the corresponding isotopic solvent) is shown.

TABLE V

Absorption band of $CHCl_3$ (1215 cm^{-1}) in $CHBr_3$							
concentration		path	shift	B	$\Delta\sigma_{\frac{1}{2}}$	$\left\lvert\frac{\Delta f(t)}{\Delta t}\right\rvert$ ($psec^{-1}$)	
$mol.l.^{-1}$	molfr.	length(μm)	$\Delta\sigma(cm^{-1})$	$(l.mol.^{-1}cm^{-2})$	(cm^{-1})	1-2 ps.	2-3 ps.
12.31	1.0	3.5	0.0	1580	8.2	0.75	0.85
6.0	0.51	9.4	0.0	1400	8.1	0.77	0.85
3.0	0.26	9.4	-0.3	1370	8.2	0.74	0.81
1.5	0.13	34.5	-0.5	1210	8.2	0.75	0.82
0.70	0.06	34.5	-0.7	1190	8.1	0.72	0.79
0.30	0.03	90.4	-0.8	1250	8.0	0.73	0.82
Absorption band of $CHCl_3$ (1215 cm^{-1}) in CS_2							
concentration		path	shift	B	$\Delta\sigma_{\frac{1}{2}}$	$\left\lvert\frac{\Delta f(t)}{\Delta t}\right\rvert$ ($psec^{-1}$)	
$mol.l.^{-1}$	molfr.	length(μm)	$\Delta\sigma(cm^{-1})$	$(l.mol.^{-1}cm^{-2})$	(cm^{-1})	1-2 ps.	2-3 ps.
12.31	1.0	3.5	0.0	1580	8.2	0.75	0.85
6.0	0.42	9.4	-1.3	1670	6.9	0.65	0.67
4.0	0.27	12.8	-1.4	1820	6.7	0.63	0.61
3.0	0.20	9.4	-1.6	1610	6.3	0.57	0.59
1.5	0.095	34.5	-1.9	1630	5.7	0.53	0.53
0.70	0.044	34.5	-2.1	1550	5.6	0.51	0.50
0.30	0.019	90.4	-2.5	1550	5.5	0.49	0.48
Absorption band of $CHCl_3$ (1215 cm^{-1}) in $c\text{-}C_6H_{12}$							
concentration		path	shift	B	$\Delta\sigma_{\frac{1}{2}}$	$\left\lvert\frac{\Delta f(t)}{\Delta t}\right\rvert$ ($psec^{-1}$)	
$mol.l.^{-1}$	molfr.	length(μm)	$\Delta\sigma(cm^{-1})$	$(l.mol.^{-1}cm^{-2})$	(cm^{-1})	1-2 ps.	2-3 ps.
12.31	1.0	3.5	0.0	1580	8.2	0.75	0.85
6.0	0.56	9.4	+0.1	1710	6.6	0.59	0.59
3.0	0.30	9.4	0.0	1620	5.9	0.52	0.52
1.5	0.16	33.4	0.0	1430	5.1	0.46	0.46
0.70	0.081	33.4	-0.3	1460	4.9	0.42	0.43
0.30	0.034	90.4	-0.7	1450	4.7	0.42	0.40

Table V. Dilution series in different solvents for $CHCl_3$.

TABLE VI

Absorption band of $CDCl_3$ (910 cm^{-1}) in CS_2							
concentration		path	shift	B	$\Delta\sigma_{\frac{1}{2}}$	$\left\lvert\frac{\Delta f(t)}{\Delta t}\right\rvert$ ($psec^{-1}$)	
$mol.l.^{-1}$	molfr.	length(μm)	$\Delta\sigma(cm^{-1})$	$(l.mol.^{-1}cm^{-2})$	(cm^{-1})	1-2 ps.	2-3 ps.
12.45	1.0	2.5	0.0	4790	14.5	1.56	2.07
5.0	0.34	4.2	-2.7	4420	10.9	1.07	1.38
4.0	0.27	4.2	-2.9	4480	10.3	0.99	1.29
2.0	0.13	12.8	-3.2	4050	9.5	0.91	1.06
0.50	0.031	33.0	-3.6	4320	8.4	0.78	0.82
0.15	0.009	91.0	-3.7	4100	8.2	0.75	0.77

Absorption band of $CDCl_3$ (910 cm^{-1}) in $c\text{-}C_6H_{12}$							
concentration		path	shift	B	$\Delta\sigma_{\frac{1}{2}}$	$\left\lvert\frac{\Delta f(t)}{\Delta t}\right\rvert$ ($psec^{-1}$)	
$mol.l.^{-1}$	molfr.	length(μm)	$\Delta\sigma(cm^{-1})$	$(l.mol.^{-1}cm^{-2})$	(cm^{-1})	1-2 ps.	2-3 ps.
12.45	1.0	2.5	0.0	4790	14.5	1.56	2.07
7.0	0.64	2.9	-1.0	3740	12.4	1.26	1.76
4.0	0.39	4.2	-1.1	5090	11.3	1.10	1.43
2.0	0.21	12.8	-1.4	4740	9.8	0.94	1.03
1.0	0.11	12.8	-1.6	4780	9.2	0.89	1.02
0.50	0.057	33.0	-1.4	4580	8.6	0.82	0.85

Absorption band of $CDCl_3$ (910 cm^{-1}) in CH_2Cl_2							
concentration		path	shift	B	$\Delta\sigma_{\frac{1}{2}}$	$\left\lvert\frac{\Delta f(t)}{\Delta t}\right\rvert$ ($psec^{-1}$)	
$mol.l.^{-1}$	molfr.	length(μm)	$\Delta\sigma(cm^{-1})$	$(l.mol.^{-1}cm^{-2})$	(cm^{-1})	1-2 ps.	2-3 ps.
12.45	1.0	2.5	0.0	4790	14.5	1.56	2.07
5.0	0.35	4.2	+0.4	5150	12.3	1.24	1.82
4.0	0.28	4.2	+0.3	5010	11.9	1.18	1.82
2.0	0.13	12.8	+0.7	4750	10.9	0.98	1.18
1.0	0.066	12.8	+0.7	4570	10.8	1.03	1.30
0.50	0.032	33.0	+0.8	4920	10.6	1.00	1.25

Table VI. Dilution series in different solvents for $CDCl_3$.

TABLE VII

Absorption band of $CHBr_3$ (1142 cm^{-1}) in CCl_4						
concentration		path	shift	B	$\Delta\sigma_{\frac{1}{2}}$	$\left\lvert\frac{\Delta f(t)}{\Delta t}\right\rvert$ ($psec^{-1}$)
$mol.l.^{-1}$	molfr.	length(μm)	$\Delta\sigma(cm^{-1})$	$(l.mol.^{-1}cm^{-2})$	(cm^{-1})	1-2 ps.
11.40	1.0	5.4	0.0	2700	12.8	1.32
7.09	0.65	9.8	+1.4	2443	10.4	1.02
5.42	0.50	9.8	+1.9	2332	9.5	0.90
4.06	0.37	9.8	+2.3	2371	8.7	0.82
2.42	0.23	9.8	+2.7	2375	7.8	0.75
0.41	0.04	90.8	+3.1	2584	6.3	0.57

Absorption band of $CHBr_3$ (1142 cm^{-1}) in $CHCl_3$						
concentration		path	shift	B	$\Delta\sigma_{\frac{1}{2}}$	$\left\lvert\frac{\Delta f(t)}{\Delta t}\right\rvert$ ($psec^{-1}$)
$mol.l.^{-1}$	molfr.	length(μm)	$\Delta\sigma(cm^{-1})$	$(l.mol.^{-1}cm^{-2})$	(cm^{-1})	1-2 ps.
11.40	1.0	5.4	0.0	2700	12.8	1.32
5.86	0.50	9.8	+1.9	2332	10.3	1.03
3.09	0.26	9.8	+2.6	2575	9.5	0.91
1.23	0.10	33.4	+3.2	2169	8.3	0.75
0.37	0.03	90.8	+3.3	2229	7.8	0.74

Absorption band of $CHBr_3$ (1142 cm^{-1}) in CH_2Cl_2						
concentration		path	shift	B	$\Delta\sigma_{\frac{1}{2}}$	$\left\lvert\frac{\Delta f(t)}{\Delta t}\right\rvert$ ($psec^{-1}$)
$mol.l.^{-1}$	molfr.	length(μm)	$\Delta\sigma(cm^{-1})$	$(l.mol.^{-1}cm^{-2})$	(cm^{-1})	1-2 ps.
11.40	1.0	5.4	0.0	2700	12.8	1.32
7.74	0.61	10.5	+1.7	2281	12.2	1.22
5.56	0.41	10.5	+2.6	2358	11.6	1.14
4.22	0.30	9.8	+3.2	2477	11.7	1.15
3.62	0.25	10.5	+3.7	2315	11.6	1.13
2.24	0.13	33.4	+3.8	2302	11.1	1.07
0.30	0.02	97.0	+4.4	2353	10.8	1.00

Table VII. Dilution series in different solvents for $CHBr_3$.

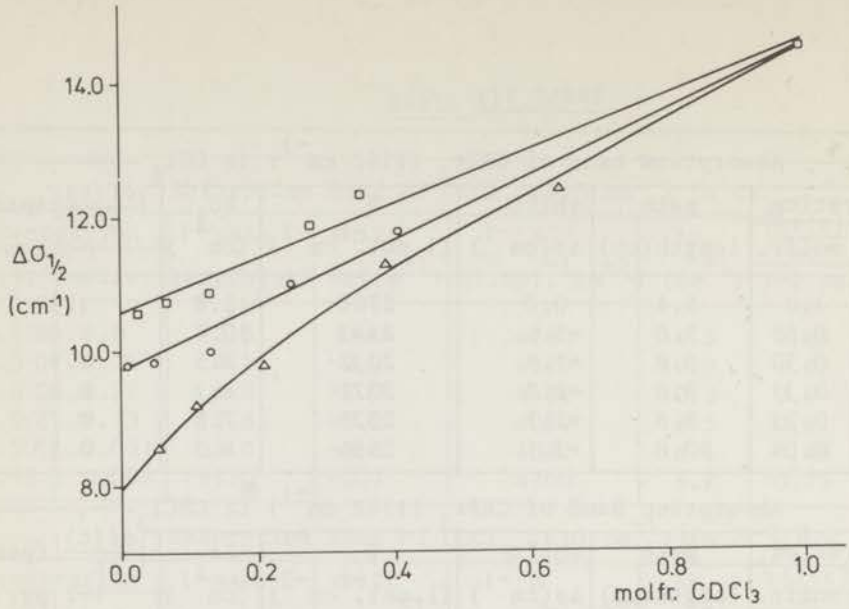

Fig.20. The concentration dependence of $\Delta\sigma_{\frac{1}{2}}$ for $CDCl_3$ (910 cm^{-1}) using different solvents. □: diluted in CH_2Cl_2, o: in $CHCl_3$, Δ: in c-C_6H_{12}.

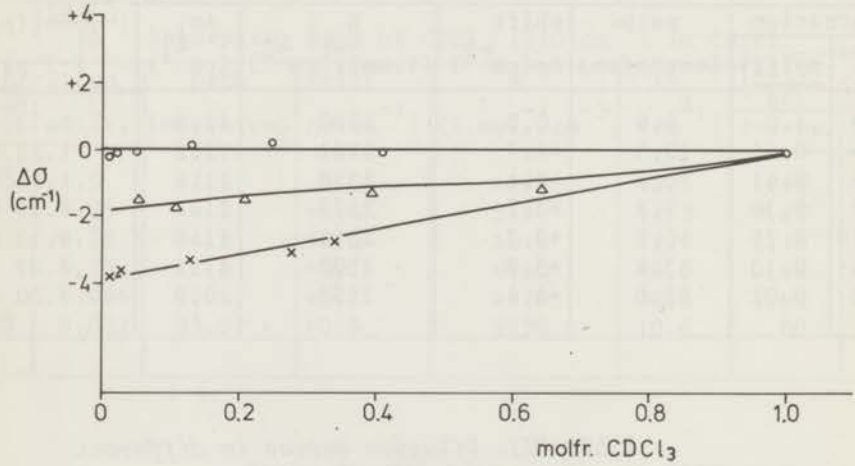

Fig.21. The concentration dependence of Δσ for $CDCl_3$ (910 cm^{-1}) using different solvents. o: diluted in $CHCl_3$, Δ: in c-C_6H_{12}, ×: in CS_2.

It may be concluded from the data presented in Table V-VII and Fig.20-21 that isotopic dilution is to be preferred, especially in view of the fact that the shift $\Delta\sigma$ is small in isotopic dilutions compared with $\Delta\sigma$ in other solutions (Fig.21). This confirms the impression that the change of the molecular environments in these solvents may complicate the extraction of the influence of intermolecular vibrational relaxation on the spectrum.

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CHAPTER IV

THEORY

1. INTRODUCTION

The purpose of this chapter is to investigate the validity of the usual assumption that dipole moment correlation functions may be separated into a vibrational and rotational correlation function (1-4). Furthermore the neglect of the temperature dependence of vibrational relaxation is discussed (1-2).

Therefore the contribution of intermolecular vibrational relaxation is estimated theoretically for a representative system, using a simple model for the liquid. In particular neat liquids having a high density of intramolecular normal modes at the same frequency facilitating intermolecular vibrational relaxation are considered.

As pointed out before (5), when absorption bands of neat liquids are compared with isotopically diluted solutions, it is possible to estimate experimentally the influence of intermolecular vibrational relaxation.

The liquid is assumed to be isotropic. The intramolecular vibrations are treated in the harmonic approximation. Effects due to the polarizability of the molecules are not taken into account explicitly.

The theoretical considerations will follow closely the linear response formalism, as presented by Kubo (6,7) to treat for example resonating spin systems. The main difficulty in the application of this type of theory to IR bandshape problems arises from the fact that whereas in NMR the nuclear spin system is space-quantized, the

vibrational degrees of freedom are not. The electric moment is fixed to the molecular frame and although at sufficiently high frequencies the oscillatory motion may be loosely coupled to the bath, the molecular motion reorients the direction of the transition dipole moment. Given an intermolecular interaction which is bath modulated, the time correlation function for the electric moment will be represented in a form, displaying the influence of the intermolecular vibrational relaxation on the unperturbed autocorrelation function. In this way, without precise knowledge of the molecular motions, the contribution of the intermolecular vibrational relaxation may be estimated theoretically if cross correlations between different mechanisms coupling the system to the bath may be neglected. It should be realized that at low frequencies ($\hbar\omega \lesssim kT$) the vibrational motion may not be sufficiently isolated to be treated as a degree of freedom which is loosely coupled to the bath.

It will be shown that the transition dipole-transition dipole interaction leads to an acceptable qualitative estimate for the intermolecular vibrational relaxation measured by the isotopic dilution method. Furthermore, the dependence of the intermolecular vibrational relaxation on the molecular reorientational motion will be explicitly formulated.

2. GENERAL THEORETICAL CONSIDERATIONS.

As is usual the imaginary part of the admittance tensor $\chi''(\omega)$ will be expressed in terms of the time evolution of the total electric moment operator $\vec{M}$ of the system under consideration (8).

$$\chi''(\omega) = \frac{\omega}{4E_\beta(\omega)} \int_{-\infty}^{+\infty} dt\, e^{-i\omega t} \left\langle \left[\vec{M}, \vec{M}(t) \right]_+ \right\rangle \tag{1}$$

Here E_β is the average energy of an oscillator with frequency ω at a temperature T:

$$E_\beta(\omega)=\frac{\hbar\omega}{2}\,\mathrm{cotgh}(\tfrac{1}{2}\beta\hbar\omega) \qquad ; \; (\beta=(kT)^{-1})$$

Confining the treatment to the dissipative response of isotropic systems to linearly polarized radiation, only the zz-component of the imaginary part of the admittance tensor will be discussed

$$\chi''_{zz}(\omega)=\frac{\omega}{4E_\beta(\omega)}\int_{-\infty}^{+\infty} dt\; e^{-i\omega t}\left\langle\left[M_z,M_z(t)\right]_+\right\rangle \tag{2}$$

The average $\langle A\rangle$ is defined as $\langle A\rangle = \mathrm{Tr}\rho A$, where ρ is the density matrix.

$\chi''_{zz}(\omega)$ is proportional to $n(\omega)k(\omega)$(9), which may be determined experimentally; $n(\omega)$ and $k(\omega)$ are the real and imaginary parts of the complex refractive index at frequency ω, respectively. For relatively narrow bands at sufficiently high frequencies $\omega/E_\beta(\omega)$ is an insensitive function of ω in the region of interest. In that case the cosine transform of $n(\omega)k(\omega)$ is proportional to the quantummechanical autocorrelation function $\Phi_{zz}(t)$ defined by

$$\Phi_{zz}(t)=\tfrac{1}{2}\left\langle\left[M_z,M_z(t)\right]_+\right\rangle \tag{3}$$

In eqn.(3) $M_z(t)$ describes the time dependence of the z-component of the electric moment operator of the system due to the complete Hamiltonian.

The Hamilton operator may be written as

$$H = E^o + F + G^o \tag{4}$$

E^o is the Hamilton operator of the intramolecular vibrational degrees of freedom of the isolated molecules. F is used to denote the Hamiltonian of all other degrees of freedom; it will be referred to as the bath Hamiltonian. G^o is the interaction Hamiltonian, coupling the intramolecular vibrational degrees of freedom to the bath.

It is convenient to rewrite the total Hamiltonian by addition of the bath averaged interaction $\langle G^o\rangle_F$ to the vibrational Hamiltonian

and subtraction of the same quantity from the interaction G^o (10)

$$H = E + F + G \tag{5}$$

Here $G = G^o - \langle G^o \rangle_F$ and $E = E^o + \langle G^o \rangle_F$ with

$$\langle G^o \rangle_F = \mathrm{Tr}_F \, e^{-\beta F} G^o \tag{6}$$

$\langle G^o \rangle_F$ is still an operator, Tr_F indicating that the trace has only been taken with respect to the bath coordinates.

The density operator ρ will be assumed to be closely approximated by the expression

$$\rho = \frac{e^{-\beta(E+F)}}{\mathrm{Tr}\, e^{-\beta(E+F)}} \tag{7}$$

This assumption is justified, if the influence of G on ρ is negligible. As G has been defined in eqn.(5) as the fluctuation of the interaction with respect to its bath average, the assumption in eqn.(7) will be valid, if these fluctuations are small. For interactions involving oscillators of sufficiently high frequency this condition will be met readily. Contrarily, the fluctuation of the coupling between permanent dipoles is not negligible with respect to kT in polar liquids at room temperature.

For any given molecule, the part of E up to and including the second order in the displacement coordinates of the nuclei of this molecule only, with respect to its centre of mass frame, may be used to define intramolecular normal coordinates Q, as usual. These normal modes will be numbered for the complete system Q_i, Q_j..., with no index to indicate the molecule in which the oscillation is localized. Anharmonicities, interoscillator interaction etc. may now be expanded using the Q_i as a basis. The normal coordinates defined in this way may differ considerably from the normal coordinates defined in the same way for the isolated molecules due to the inclusion of $\langle G^o \rangle_F$ in E.

To study the effect of small interactions on the liquid state spectrum the normal modes defined in this way constitute a convenient basis. Now the potential energy V_E included in E may be expressed as:

$$2V_E = \sum_i \lambda_i Q_i^2 + \sum_{i \neq j} \langle C_{ij} \rangle_F Q_i Q_j + \ldots\ldots\ldots \tag{8}$$

Of course $\langle C_{ij} \rangle_F \neq 0$ implies that Q_i and Q_j are situated on different molecules. This coupling coefficient introduces a second order shift which will be neglected together with higher order terms in V_E: for the calculation of the intermolecular vibrational relaxation rate the intramolecular oscillators will be assumed to be harmonic. For low frequency modes ($\lesssim 200\ cm^{-1}$) the definition of E and the harmonicity approximation will not usually be physically meaningfull. The influence of inhomogeneous broadening will not be treated here: in this case the system must be treated as an inhomogeneous collection of subsystems leading to a distribution function for each λ_i.

G can now be expanded as

$$G = \sum_i (k_i - \langle k_i \rangle_F) Q_i + \sum_i (k_{ii} - \langle k_{ii} \rangle_F) Q_i^2 + \sum_{i<j} (k_{ij} - \langle k_{ij} \rangle_F) Q_i Q_j + \ldots \tag{9}$$

The fluctuations in the interaction may be divided:

$$G = G_1 + G_2 \tag{10}$$

where

$$G_2 = \sum_{i<j} (C_{ij} - \langle C_{ij} \rangle_F) Q_i Q_j \tag{11}$$

In eqn.(10) G_2 is defined to contain only the interactions between normal coordinates in different molecules, while all other interactions involving normal modes are contained in G_1.

By the definition of E^o the operators E^o and F commute; $[E^o, F]_- = 0$.

Because evidently $\left[\langle G^o \rangle_F, F\right]_- = 0$, it follows immediately, that

$$\left[E,F\right]_- = 0 \tag{12}$$

The assumption stated in eqn.(7) combined with eqn.(12) allows independent averaging procedures over vibrational and bath coordinates respectively.

Using the definition $A^{\times}B = \left[A,B\right]_-$ and the identity $e^{A^{\times}} B = e^{A}Be^{-A}$, $M_z(t)$ can be written as

$$M_z(t)=e^{i/\hbar(E+F+G)^{\times}t}M_z = \exp_o(i/\hbar \int_o^t dt'\ \bar{\bar{G}}^{\times}(t'))\ \bar{\bar{M}}_z(t) \tag{13}$$

where $\exp_o$ indicates a time-ordered exponential.
In this expression the double bar means that the operators are written in the interaction representation under E and F. In the following treatment a single bar indicates the interaction representation under F

$$e^{i/\hbar(E+F)^{\times}t}\ M_z \equiv e^{i/\hbar E^{\times}t}\ \bar{M}_z(t) \equiv \bar{\bar{M}}_z(t) \tag{14}$$

Using (13) $\Phi_{zz}(t)$ can be written in a form suitable for perturbation expansion

$$\Phi_{zz}(t) = \tfrac{1}{2}\left\langle\left[M_z,\ \exp_o(i/\hbar \int_o^t dt'\ \bar{\bar{G}}^{\times}(t'))\ \bar{\bar{M}}_z(t)\right]_+\right\rangle \tag{15}$$

The motion of $\bar{\bar{M}}_z(t)$ under the influence of E will now be written in a spectral resolution using an eigenbasis of E. Each microscopic transition moment contained in $\bar{\bar{M}}_z(t)$ will be assumed to be proportional to the normal coordinate involved. The resulting spectral components are time dependent due to F only. The components of the spectral resolution of the normal coordinate Q_l will be denoted $Q_l^{\alpha l}$. Explicitly this results in

$$\bar{M}_z(t) = \bar{M}_z^o(t) + \sum_l \left(\frac{\partial \bar{\bar{M}}(t)}{\partial Q_l}\right)_z^{(o)} Q_l(t) = \bar{M}_z^o(t) + \sum_l \left(\frac{\partial \vec{\mu}(t)}{\partial Q}\right)_{l,z} Q_l(t)$$

$$= \bar{M}_z^o(t) + \sum_l \sum_{\alpha_l} \left(\frac{\partial \vec{\mu}(t)}{\partial Q}\right)_{l,z} Q_l^{\alpha_l} e^{i\alpha_l t}$$

$$= \bar{M}_z^o(t) + \sum_\alpha \{\sum_l \left(\frac{\partial \vec{\mu}(t)}{\partial Q}\right)_{l,z} Q_l^{\alpha_l}\}_{\alpha_l=\alpha} e^{i\alpha t}$$

$$= \bar{M}_z^o(t) + \sum_\alpha \bar{M}_z^\alpha(t) e^{i\alpha t} = \sum_\omega \bar{M}_z^\omega(t) e^{i\omega t} \tag{16}$$

In the last summation the permanent moment ($\omega=0$) is included for convenience. Furthermore it is implicitly assumed in eqn.(16) that $\left(\frac{\partial \bar{\bar{M}}(t)}{\partial Q_l}\right)_z^{(o)} = \left(\frac{\partial \vec{\mu}(t)}{\partial Q}\right)_{l,z}$, where μ is the dipole moment of the molecule at which the normal mode Q_l is localized.

The study of the absorption spectrum is, in the present context, always confined to one particular band centred at frequency α_0. If such an absorption band is isolated from other bands in the spectrum it is mainly determined by $\Phi_{zz}^{\alpha_0}(t)$ involving the two spectral components ($\alpha=\pm\alpha_0$) of the normal modes with frequency α_0 (7)

$$\Phi_{zz}^{\alpha_0}(t) = \tfrac{1}{2}\left\langle\left[M_z^{-\alpha_0}, \exp_o\left(\tfrac{i}{\hbar}\int_o^t dt'\bar{\bar{G}}^\times(t')\right)\bar{M}_z^{\alpha_0}(t)\right]_+\right\rangle e^{i\alpha_0 t} \tag{17}$$

$\Phi_{zz}^{\alpha_0}(t)$ is now written in the form of a dimensionless average involving the exponential $\exp_o\left(\tfrac{i}{\hbar}\int_o^t dt'\,\bar{\bar{G}}^\times(t')\right)$, because in this form it is suitable for application of the cumulant expansion theorem (7). In order to arrive at this form $\Phi_{zz}^{\alpha_0}(t)$ is divided by the zero order autocorrelation function $\Phi_{zz}^o(t)$ defined by

$$\Phi_{zz}^o(t) = \tfrac{1}{2}\left\langle\left[M_z^{-\alpha_0}, \bar{M}_z^{\alpha_0}(t)\right]_+\right\rangle e^{i\alpha_0 t} \tag{18}$$

Dividing (17) by (18) and rearranging yields

$$\Phi_{zz}^{\alpha_0}(t) = \Phi_{zz}^o(t)\frac{\left\langle\left[M_z^{-\alpha_0}, \exp_o\left(\tfrac{i}{\hbar}\int_o^t dt'\bar{\bar{G}}^\times(t')\right)\bar{M}_z^{\alpha_0}(t)\right]_+\right\rangle}{\left\langle\left[M_z^{-\alpha_0}, \bar{M}_z^{\alpha_0}(t)\right]_+\right\rangle}$$

$$\Phi_{zz}^{\alpha_0}(t) \equiv \Phi_{zz}^o(t)\left\langle\left\langle\exp_o\left(\tfrac{i}{\hbar}\int_o^t dt'\bar{\bar{G}}^\times(t')\right)\right\rangle\right\rangle \tag{19}$$

Application of the cumulant expansion theorem to (19) gives to second order

$$\Phi^{\alpha_0}_{zz}(t)=\Phi^{o}_{zz}(t)\exp\left[{}^{i}/_{\hbar}\int_0^t dt'\left\langle\left\langle\bar{\bar{G}}^{\times}(t')\right\rangle\right\rangle_c + -{}^{1}/_{\hbar^2}\int_0^t dt'\int_0^{t'} dt''\left\langle\left\langle\bar{\bar{G}}^{\times}(t'')\bar{\bar{G}}^{\times}(t')\right\rangle\right\rangle_c\right] \tag{20}$$

Substituting eqn.(10) for G and assuming as a first approximation that G_1 and G_2 are statistically uncorrelated in the sense defined by the averaging procedure introduced in eqn.(19) (i.e. all cross terms of G_1 and G_2 in the cumulant expansion will vanish (11)) $\Phi^{\alpha_0}_{zz}(t)$ can be written as

$$\Phi^{\alpha_0}_{zz}(t)=\Phi^{o}_{zz}(t)\exp\left[{}^{i}/_{\hbar}\int_0^t dt'\left\langle\left\langle\bar{\bar{G}}_1^{\times}(t')+\bar{\bar{G}}_2^{\times}(t')\right\rangle\right\rangle_c + -{}^{1}/_{\hbar^2}\int_0^t dt'\int_0^{t'} dt''\left\langle\left\langle\bar{\bar{G}}_1^{\times}(t'')\bar{\bar{G}}_1^{\times}(t')+\bar{\bar{G}}_2^{\times}(t'')\bar{\bar{G}}_2^{\times}(t')\right\rangle\right\rangle_c\right] \tag{21}$$

Now it is supposed that it is experimentally possible to suppress the influence of G_2 on $\Phi^{\alpha_0}_{zz}(t)$ without changing the physical environment of the molecules in the system in any other way. Then it is easy to see that the autocorrelation function is changed to

$$\Phi^{\alpha_0^0}_{zz}(t)=\Phi^{o}_{zz}(t)\exp\left[{}^{i}/_{\hbar}\int_0^t dt'\left\langle\left\langle\bar{\bar{G}}_1^{\times}(t')\right\rangle\right\rangle_c + -{}^{1}/_{\hbar^2}\int_0^t dt'\int_0^{t'} dt''\left\langle\left\langle\bar{\bar{G}}_1^{\times}(t'')\bar{\bar{G}}_1^{\times}(t')\right\rangle\right\rangle_c\right] \tag{22}$$

Dividing eqn.(21) by eqn.(22) the following expression for $\Phi^{\alpha_0}_{zz}(t)$ is obtained

$$\Phi^{\alpha_0}_{zz}(t)=\Phi^{\alpha_0^0}_{zz}(t)\exp\left[{}^{i}/_{\hbar}\int_0^t dt'\left\langle\left\langle\bar{\bar{G}}_2^{\times}(t')\right\rangle\right\rangle_c + -{}^{1}/_{\hbar^2}\int_0^t dt'\int_0^{t'} dt''\left\langle\left\langle\bar{\bar{G}}_2^{\times}(t'')\bar{\bar{G}}_2^{\times}(t')\right\rangle\right\rangle_c\right] \tag{23}$$

It is important to note here that the neglect of cross correlations leading to eqn.(21) is essential in the derivation of eqn.(23) where the influence of a part of the coupling between system and bath on the correlation function is shown explicitly. Although the importance of this approximation cannot be estimated in general it will be assumed that the main effect of G_2 is contained in the autocorrelation.

The first order term in the exponent of eqn.(23) is a rather complicated average value of the fluctuation of G_2^o. Due to the

approximation introduced with eqn.(7), both $\langle G_2^o \rangle_F$ and $\langle\langle \bar{\bar{G}}_2^{\times}(t') \rangle\rangle$ will vanish if G_2 represents any electrostatic intermolecular interaction between molecules bearing no net charge. Only these interactions will be considered here and the first order term may therefore be omitted. As a consequence the second order cumulant average reduces to a normal average in the sense of eqn.(19),

$$\begin{aligned}\Phi_{zz}^{\alpha_0}(t) &= \Phi_{zz}^{\alpha_0 0}(t)\ \exp\left[-{}^1/_{\hbar^2}\ {}_o\!\int^t dt'\ {}_o\!\int^{t'} dt''\langle\langle \bar{\bar{G}}_2^{\times}(t'')\bar{\bar{G}}_2^{\times}(t')\rangle\rangle_c\right] \\ &= \Phi_{zz}^{\alpha_0 0}(t)\ \exp\left[-{}^1/_{\hbar^2}\ {}_o\!\int^t dt'\ {}_o\!\int^{t'} dt''\langle\langle \bar{\bar{G}}_2^{\times}(t'')\bar{\bar{G}}_2^{\times}(t')\rangle\rangle\right]\end{aligned} \tag{24}$$

For ease of notation the function F(t) is defined as

$$F(t) = \exp\left[-{}^1/_{\hbar^2}\ {}_o\!\int^t dt'\ {}_o\!\int^{t'} dt''\langle\langle \bar{\bar{G}}_2^{\times}(t'')\bar{\bar{G}}_2^{\times}(t')\rangle\rangle\right] \tag{25}$$

Using the averaging procedure as defined in eqn.(19)

$$F(t) = \exp\left[\frac{-{}^1/_{\hbar^2}\ {}_o\!\int^t dt'\ {}_o\!\int^{t'} dt''\left\langle\left[M_z^{-\alpha_0},\left[\bar{\bar{G}}_2(t''),\left[\bar{\bar{G}}_2(t'),\bar{M}_z^{\alpha_0}(t)\right]_-\right]_-\right]_+\right\rangle}{\left\langle\left[M_z^{-\alpha_0},\bar{M}_z^{\alpha_0}(t)\right]_+\right\rangle}\right] \tag{26}$$

$\bar{M}_z^{\alpha_0}(t)$, the component with frequency α_0 of the spectral resolution of the macroscopic dipole moment operator, is now written as a sum over microscopic transition dipole moments using eqn.(16)

$$\bar{M}_z^{\alpha_0}(t) = \sum_l \cos\theta_l(t)\left(\frac{\partial\mu}{\partial Q}\right)_l Q_l^{\alpha_0} \tag{27}$$

In this expression the direction cosine $\cos\theta_l(t)$ of the microscopic transition moment, defined with respect to a laboratory fixed frame, moves under F.

In the same way $\bar{\bar{G}}_2(t)$ can be written as

$$\bar{\bar{G}}_2(t) = \sum_{i<j}\ \sum_{\beta_i\beta_j} (C_{ij}(t) - \langle C_{ij}(t)\rangle_F) Q_i^{\beta_i} Q_j^{\beta_j} e^{i(\beta_i+\beta_j)t} \tag{28}$$

The time dependent function $(C_{ij}(t) - \langle C_{ij}(t)\rangle_F)$ is the part of $\bar{\bar{G}}_2(t)$

which moves under F, while $e^{i(\beta_i+\beta_j)t}$ describes the time dependence due to E. For convenience in notation the time dependent function $\overline{C}_{ij}(t)$ is defined

$$\overline{C}_{ij}(t) \equiv (C_{ij}(t) - \langle C_{ij}(t)\rangle_F) \tag{29}$$

Substituting (27), (28) and (29) in eqn.(26) yields

$$F(t)=\exp\left[\frac{-1}{N(t)\hbar^2}\int_0^t dt'\int_0^{t'} dt'' \sum_{i<j}\sum_{p<q}\sum_{k,l}\sum_{\beta_i\beta_j}\sum_{\gamma_p\gamma_q}\left\langle \cos\theta_k(0)\cos\theta_l(t)\times\right.\right.$$
$$\times\left(\frac{\partial\mu}{\partial Q}\right)_k\left(\frac{\partial\mu}{\partial Q}\right)_l \overline{C}_{ij}(t'')\overline{C}_{pq}(t')\left[Q_k^{-\alpha_0},\left[Q_i^{\beta_i}Q_j^{\beta_j},\left[Q_p^{\gamma_p}Q_q^{\gamma_q},Q_l^{\alpha_0}\right]_-\right]_-\right]_+ \times$$
$$\left.\left.\times\, e^{i(\beta_i+\beta_j)t''}e^{i(\gamma_p+\gamma_q)t'}\right\rangle\right] \tag{30}$$

in which N(t) can be written as

$$N(t)=\sum_{k,l}\left\langle \cos\theta_k(0)\cos\theta_l(t)\left(\frac{\partial\mu}{\partial Q}\right)_k\left(\frac{\partial\mu}{\partial Q}\right)_l\left[Q_k^{-\alpha_0},Q_l^{\alpha_0}\right]_+\right\rangle \tag{31}$$

The expression for F(t) is now simplified by using the following rules;

a) $C_{jj}(t) \equiv 0$

b) Each commutator should contain the same normal coordinate twice.

c) Each normal coordinate must appear an even number of time in the anticommutator.

d) The frequency components should fulfill the following relation: $-\alpha_0+\beta_i+\beta_j+\gamma_p+\gamma_q+\alpha_0 = 0$. This condition is only valid under the assumption in eqn.(7).

Using these rules the eqn.(30) and (31) become

$$F(t)=\exp\left[\frac{-1}{N(t)\hbar^2}\int_0^t dt'\int_0^{t'} dt''\sum_{k,l}\sum_{\beta}\left\langle\cos\theta_l(0)\cos\theta_l(t)\left(\frac{\partial\mu}{\partial Q}\right)_l^2\overline{C}_{lk}(t'')\overline{C}_{lk}(t')\times\right.\right.$$
$$\left.\left.\times\left[Q_l^{-\alpha_0},\left[Q_l^{\alpha_0}Q_k^{\beta},\left[Q_k^{-\beta}Q_l^{-\alpha_0},Q_l^{\alpha_0}\right]_-\right]_-\right]_+ e^{i(\alpha_0+\beta)t''}e^{i(-\alpha_0-\beta)t'}\right\rangle\right] \tag{32}$$

and

$$N(t)=\sum_{l}\left\langle \cos\theta_l(0)\cos\theta_l(t)\left(\frac{\partial\mu}{\partial Q}\right)_l^2\left[Q_l^{-\alpha_0},Q_l^{\alpha_0}\right]_+\right\rangle \tag{32a}$$

In eqn.(32) terms depending on three different normal modes, have been neglected.

As the treatment is confined to harmonic oscillators, the summation over β consists of two terms only; ($\beta=\pm\beta_0$). Because the adiabatic or near-adiabatic perturbations are most important, only one term contributes i.e. the term making $(\alpha_0+\beta)$ as small as possible. After performing the summation over β and averaging the system operators over the vibrational states (12), the result is finally

$$F(t)=\exp\left[\frac{-1}{N(t)\hbar^2}\int_0^t dt'\int_0^{t'} dt''\sum_{l,k}\left\langle \cos\theta_l(0)\cos\theta_l(t)\left(\frac{\partial\mu}{\partial Q}\right)_l^2\overline{C}_{lk}(t'')\overline{C}_{lk}(t')\times\right.\right.$$
$$\left.\left.\times\frac{\hbar^3}{8\alpha_0^2\beta_0}\,\mathrm{cotgh}(\tfrac{1}{2}\beta\hbar\alpha_0)\right\rangle e^{i(\alpha_0-\beta_0)(t''-t')}\right] \tag{33}$$

with

$$N(t)=\sum_{l}\left\langle \cos\theta_l(0)\cos\theta_l(t)\left(\frac{\partial\mu}{\partial Q}\right)_l^2\frac{\hbar}{2\alpha_0}\,\mathrm{cotgh}(\tfrac{1}{2}\beta\hbar\alpha_0)\right\rangle \tag{34}$$

This result is now applied to a specific example of the interaction G_2.

3. APPLICATION OF THE THEORY

An example of the interaction G_2 is the transition dipole-transition dipole coupling G_{dip}, defined as (13,14)

$$G_{dip}(t)=\sum_{i<j}\sum_{\beta_i\beta_j}\left(\frac{\partial\mu}{\partial Q}\right)_i\left(\frac{\partial\mu}{\partial Q}\right)_j\sum_{m,m'}\frac{a^{mm'}Y_1^m(\Omega_t^i)Y_1^{m'}(\Omega_t^j)Y_2^{-m-m'}(\Omega_t^{rij})}{r_{ij}^3(t)}\cdot$$
$$Q_i^{\beta_i}Q_j^{\beta_j}e^{i(\beta_i+\beta_j)t} \tag{35}$$

In this equation the functions $Y_1^m(\Omega_t^i)$, $Y_1^{m'}(\Omega_t^j)$ and $Y_2^{-m-m'}(\Omega_t^{r_{ij}})$ are the spherical harmonics, determined by the orientation of the transition dipole moments i and j and the distance vector $\vec{r}_{ij}$ of the oscillators i and j at a given time t in a laboratory fixed frame. The quantity $a^{mm'}$ is a constant factor, dependent on the values of m and m'. It has been listed in Table I for the values of m and m' of interest presently.

TABLE I

	m'=1	m'=0	m'=-1
m=1	$-\frac{8\pi}{3}\left(\frac{6\pi}{5}\right)^{\frac{1}{2}}$	$\frac{8\pi}{3}\left(\frac{3\pi}{5}\right)^{\frac{1}{2}}$	$-\frac{8\pi}{3}\left(\frac{\pi}{5}\right)^{\frac{1}{2}}$
m=0	$\frac{8\pi}{3}\left(\frac{3\pi}{5}\right)^{\frac{1}{2}}$	$-\frac{16\pi}{3}\left(\frac{\pi}{5}\right)^{\frac{1}{2}}$	$\frac{8\pi}{3}\left(\frac{3\pi}{5}\right)^{\frac{1}{2}}$
m=-1	$-\frac{8\pi}{3}\left(\frac{\pi}{5}\right)^{\frac{1}{2}}$	$\frac{8\pi}{3}\left(\frac{3\pi}{5}\right)^{\frac{1}{2}}$	$-\frac{8\pi}{3}\left(\frac{6\pi}{5}\right)^{\frac{1}{2}}$

Table I. Values of $a^{mm'}$ as function of m and m'.

Considering the definition of $\overline{\overline{G}}_2(t)$ in eqn.(28) the factor $C_{ij}(t)$ is in the case of G_{dip}:

$$C_{ij}(t)=\sum_{m,m'}\frac{a^{mm'}Y_1^m(\Omega_t^i)Y_1^{m'}(\Omega_t^j)Y_2^{-m-m'}(\Omega_t^{r_{ij}})}{r_{ij}^3(t)}\left(\frac{\partial\mu}{\partial Q}\right)_i\left(\frac{\partial\mu}{\partial Q}\right)_j \tag{36}$$

It is assumed that the transition dipole moment vectors are placed in the centres of gravity of the molecules. Furthermore the assumption of isotropical rotational diffusion for the molecular reorientation is made. Using this model the averaging procedures over the orientations of the transition dipole moments i and j, and the distance vector $\vec{r}_{ij}$ can be performed independent of each other.

Now it is easy to show that the bath average of $C_{ij}(t)$ is zero and therefore $\overline{C_{ij}}(t)$ as defined in eqn.(29) equals $C_{ij}(t)$ in this treatment.

$$\overline{C}_{ij}(t) = C_{ij}(t) \tag{37}$$

Substituting eqn.(36) and (37) in eqn.(34) and (33) and writing $\cos\theta_1(0)$ and $\cos\theta_1(t)$ as spherical harmonics the following result is obtained

$$F(t)=\exp\left[\frac{-1}{\overline{N}(t)}\int_0^t dt'\int_0^{t'} dt''\sum_k\left\langle Y_1^o(\Omega_o^1)Y_1^o(\Omega_t^1)\left(\frac{\partial\mu}{\partial Q}\right)_k^2\left(\frac{\partial\mu}{\partial Q}\right)_1^2\sum_{m,m'}\sum_{\mu,\mu'}a^{mm'}a^{\mu\mu'}\times\right.$$

$$\times\frac{Y_1^m(\Omega_{t''}^1)Y_1^{m'}(\Omega_{t''}^k)Y_2^{-m-m'}(\Omega_{t''}^{rk1})Y_1^{\mu}(\Omega_{t'}^1)Y_1^{\mu'}(\Omega_{t'}^k)Y_2^{-\mu-\mu'}(\Omega_{t'}^{rk1})}{r_{k1}^3(t'')\qquad\qquad r_{k1}^3(t')}\times \tag{38}$$

$$\left.\times\frac{1}{4\alpha_0\beta_0}\right\rangle e^{i(\alpha_0-\beta_0)(t''-t')}\Bigg]$$

in which

$$\overline{N}(t)=\left\langle Y_1^o(\Omega_o^1)Y_1^o(\Omega_t^1)\right\rangle \tag{38a}$$

As this investigation is restricted to isolated absorption bands only the interaction between identical oscillators will be considered. For identical oscillators: $\left(\frac{\partial\mu}{\partial Q}\right)_k \equiv \left(\frac{\partial\mu}{\partial Q}\right)_1$ and $\alpha_0=\beta_0$. This gives the following expression for F(t)

$$F(t)=\exp\left[\frac{-1}{\overline{N}(t)}\int_0^t dt'\int_0^{t'} dt''\sum_k\left\langle Y_1^o(\Omega_o^1)Y_1^o(\Omega_t^1)\left(\frac{\partial\mu}{\partial Q}\right)_1^4\sum_{m,m'}\sum_{\mu,\mu'}a^{mm'}a^{\mu\mu'}\times\right.\right. \tag{39}$$

$$\left.\left.\times\frac{Y_1^m(\Omega_{t''}^1)Y_1^{m'}(\Omega_{t''}^k)Y_2^{-m-m'}(\Omega_{t''}^{rk1})Y_1^{\mu}(\Omega_{t'}^1)Y_1^{\mu'}(\Omega_{t'}^k)Y_2^{-\mu-\mu'}(\Omega_{t'}^{rk1})}{r_{k1}^3(t'')\qquad\qquad r_{k1}^3(t')}\cdot\frac{1}{4\alpha_0^2}\right\rangle\right]$$

in which $\overline{N}(t)$ is defined by eqn.(38a).

Because the time scale of interest of autocorrelation functions, obtained from IR-absorption bands is 0-3 psec, translational diffusion is neglected in first approximation. Using the well-known orthogonality properties of spherical harmonic functions (15), this results in the following expression for the r_{k1}-dependent part in eqn.(39)

$$\sum_k \left\langle \frac{Y_2^{-m-m'}(\Omega_{t''}^{rk1})Y_2^{-\mu-\mu'}(\Omega_{t'}^{rk1})}{r_{k1}^3(t'')\quad r_{k1}^3(t')} \right\rangle = \frac{N}{3d^3}\,\delta_{-m-m',\mu+\mu'}\,(-1)^{\mu+\mu'} \tag{40}$$

In eqn. (40) N is the number density of identical oscillators and d is the distance of closest approach between two oscillators.

Now the averaging over the orientation of the oscillator l in $\bar{N}(t)$ and the orientation of the oscillator k in F(t) is performed by using the isotropic rotational diffusion model (16). In this way the part of F(t) dependent on the orientation of the oscillator k can be written as

$$\left\langle Y_l^{m'}(\Omega_{t''}^k)Y_l^{\mu'}(\Omega_{t'}^k)\right\rangle = \frac{1}{4\pi}\,e^{-|t'-t''|/\tau_l}\,\delta_{m',-\mu'}\,(-1)^{\mu'} \tag{41}$$

The result for $\bar{N}(t)$ is therefore

$$\bar{N}(t) = \frac{1}{4\pi}\,e^{-|t|/\tau_l} \tag{42}$$

Considering only identical oscillators the same value of τ_l is obtained both for the oscillator k and for the oscillator l.

Finally the function $\{Y_l^o(\Omega_0^l)Y_l^m(\Omega_{t''}^l)Y_l^\mu(\Omega_{t'}^l)Y_l^o(\Omega_t^l)\}$ of the oscillator l has to be averaged. This is performed by using the conditional probability P(o;t";t';t) for the orientation Ω_t^l of the oscillator l at t, if its orientation at the preceding times t', t" and t=0 is given by $\Omega_{t'}^l$, $\Omega_{t''}^l$ and Ω_0^l respectively. In the case of isotropic rotational diffusion this probability is given by

$$P(0;t'';t';t) = \frac{1}{4\pi}\sum_{\bar{l},\bar{m}} \overset{*}{Y}{}_{\bar{l}}^{\bar{m}}(\Omega_0^l)Y_{\bar{l}}^{\bar{m}}(\Omega_{t''}^l)e^{-|t''|/\tau_{\bar{l}}} \sum_{\bar{\bar{l}},\bar{\bar{m}}} \overset{*}{Y}{}_{\bar{\bar{l}}}^{\bar{\bar{m}}}(\Omega_{t''}^l)Y_{\bar{\bar{l}}}^{\bar{\bar{m}}}(\Omega_{t'}^l)e^{-|t'-t''|/\tau_{\bar{\bar{l}}}} \times$$
$$\times \sum_{\bar{\bar{\bar{l}}},\bar{\bar{\bar{m}}}} \overset{*}{Y}{}_{\bar{\bar{\bar{l}}}}^{\bar{\bar{\bar{m}}}}(\Omega_{t'}^l)Y_{\bar{\bar{\bar{l}}}}^{\bar{\bar{\bar{m}}}}(\Omega_t^l)e^{-|t-t'|/\tau_{\bar{\bar{\bar{l}}}}} \tag{43}$$

The result of the averaging procedure is, expressed in Clebsch-Gordan coefficients $C(l_1 l_2 l_3; m_1 m_2 m_3)$ (15)

$$\left\langle Y_1^o(\Omega_0^1)Y_1^m(\Omega_{t''}^1)Y_1^\mu(\Omega_{t'}^1)Y_1^o(\Omega_t^1)\right\rangle = \frac{3}{16\pi^2}\, e^{-\{|t''|+|t-t'|\}/\tau_1} \times$$

$$\times \sum_{\bar{\bar{l}},\bar{\bar{m}}} C(11\bar{\bar{l}};0m\bar{\bar{m}})C(11\bar{\bar{l}};000)C(\bar{\bar{l}}11;\bar{\bar{m}}\mu 0)C(\bar{\bar{l}}11;000)e^{-|t'-t''|/\tau_{\bar{\bar{l}}}}\delta_{m,\bar{\bar{m}}}\delta_{\bar{\bar{m}},-\mu} \tag{44}$$

Substituting eqn.(44).(42),(41) and (40) in eqn.(39) F(t) reduces to:

$$F(t)=\exp\left[\frac{-2\pi N\left(\frac{\partial\mu}{\partial Q}\right)_1^4}{27\alpha_0^2 d^3}\int_0^t dt'\int_0^{t'} dt''\{1 + 2e^{-|t'-t''|/\tau_2}\}\right] \tag{45}$$

In this equation τ_2 is the correlation time of the second order Legendre polynomial, which may in favorable cases be determined by NMR spectroscopy. Performing the two time integrals in eqn.(45), F(t) becomes

$$F(t)=\exp\left[-A\{\tfrac{1}{2}t^2 + 2\tau_2\{|t| + \tau_2(e^{-|t|/\tau_2} - 1)\}\}\right] \tag{46}$$

in which

$$A \equiv \frac{2\pi N\left(\frac{\partial\mu}{\partial Q}\right)_1^4}{27\alpha_0^2 d^3} \tag{46a}$$

Now it is possible to obtain an expression for measured isotopic dilution effects (5) under the assumption that transition dipole-transition dipole interaction is responsible for the entire effect. The cosine transform of $n(\omega)k(\omega)$ around the frequency α_0, obtainable from IR data will be denoted with C(t). For an isolated symmetrical absorption band at α_0 C(t) should be proportional to $\Phi_{zz}^{\alpha_0}(t)$ and therefore:

$$\ln F(t)=\ln \Phi_{zz}^{\alpha_0}(t) - \ln \Phi_{zz}^{\overset{0}{\alpha_0}}(t)=\ln C(t) - \ln C^o(t)$$
$$=-A\{\tfrac{1}{2}t^2+2\tau_2\{|t|+\tau_2(e^{-|t|/\tau_2} - 1)\}\} \tag{47}$$

Because it is usual to discuss ln C(t) rather than C(t) eqn.(47) has been presented in logarithmic form.

In an actual experiment G_2 might be eliminated by the isotopic dilution method (5). An intramolecular normal mode is then isolated from intermolecular interaction because in its substituted neighbours there is no mode at this frequency.

In eqn.(47) $C^o(t)$ is the IR correlation function at infinite isotopic dilution that may be determined by extrapolation from a dilution series. Small experimental shifts on isotopic dilution are suppressed by taking the transform with respect to the bandmaximum for each solution. The theory in its present approximation does not predict shifts for the interaction considered. However, small experimental shifts ($\sim 1\ cm^{-1}$) do not invalidate the description of the relaxation with eqn.(47) because theoretically such a shift may be suppressed by a redefinition of E with no appreciable change in A.

It is clear that eqn.(47) confirms qualitatively the main conclusions drawn from the experimental data. The dependence of ln F(t) on τ_2 obviously agrees with the experimentally observed temperature dependence of the isotopic dilution effect. Furthermore the theoretical expression predicts that the isotopic dilution effect depends on the integrated absorption intensity B (represented by $\left(\frac{\partial\mu}{\partial Q}\right)^4$ and is proportional with the concentration (N in eqn.46a). A quantitative comparison between the theory and the experimental data is given in Ch.V.

4. DISCUSSION OF THE THEORY

The main result of the present treatment is the explicit dependence of the vibrational correlation function F(t) on the reorientational motions of the molecules. It must be concluded that motional narrowing may influence IR bandshapes significantly. As F(t) is temperature dependent it is clear, that it is incorrect to assume the existence of a temperature independent "intrinsic" vibrational contribution to the lineshape (1,2). This implies that the correction procedure, based on this assumption, to obtain a

rotational correlation function is unjustified.

Now, it can explicitly be shown that an a priori separation of the time correlation function into independent reorientational and vibrational factors yields a considerably different expression. This is illustrated by applying the usually performed separation (1,2,3,4) on $\Phi_{zz}^{\alpha_0}(t)$, as given in eqn.(17). Using eqn.(16) $\Phi_{zz}^{\alpha_0}(t)$ becomes then

$$\Phi_{zz}^{\alpha_0}(t)=\tfrac{1}{2}\sum_{l,k}\left\langle\left(\frac{\partial\vec{\mu}(0)}{\partial Q}\right)_{k,z}\left(\frac{\partial\vec{\mu}(t)}{\partial Q}\right)_{l,z}\right\rangle\left\langle\left[Q_k^{-\alpha_0},\exp_o\left(\tfrac{i}{\hbar}\int_o^t dt'\bar{\bar{G}}^{\times}(t')\right)Q_l^{\alpha_0}\right]_+\right\rangle e^{i\alpha_0 t} \tag{48}$$

Eqn.(48) explicitly shows, that the separation of the correlation function into two independent parts, includes the assumption that $\bar{\bar{G}}^{\times}(t')$ is statistically uncorrelated with $\left(\frac{\partial\vec{\mu}(0)}{\partial Q}\right)_{kz}$ and $\left(\frac{\partial\vec{\mu}(t)}{\partial Q}\right)_{lz}$. Writing $\Phi_{zz}^{\alpha_0}(t)$ as defined in eqn.(48), in the form of a dimensionless average involving $\exp_o(i/\hbar\int_o^t dt'\bar{\bar{G}}^{\times}(t'))$ (dividing by $\left\langle\left[Q_k^{-\alpha_0},\ Q_l^{\alpha_0}\right]_+\right\rangle$), subsequently applying the cumulant expansion theorem and assuming that G_1 and G_2 are uncorrelated, it can be shown after some rearranging that

$$F(t)=\exp\left[\frac{-\tfrac{1}{\hbar^2}\int_o^t dt'\int_o^{t'} dt''\left\langle\left[Q_l^{-\alpha_0},\left[\bar{\bar{G}}_2(t''),\left[\bar{\bar{G}}_2(t'),Q_l^{\alpha_0}\right]_-\right]_-\right]_+\right\rangle}{\left\langle\left[Q_l^{-\alpha_0},Q_l^{\alpha_0}\right]_+\right\rangle}\right] \tag{49}$$

In the case of transition dipole-transition dipole interaction, application of eqn.(49) gives

$$\ln F(t)= -\tfrac{3}{2}\,A\tau_1\{|t| + \tfrac{1}{2}\tau_1(e^{-2|t|/\tau_1} -1)\} \tag{50}$$

where A is defined by eqn.(46a) and τ_1 is the correlation time of the first order Legendre polynomial.

Comparison of eqn.(50) and eqn.(47) immediately shows, that the assumption of neglecting the correlation between $\left(\frac{\partial\vec{\mu}(t)}{\partial Q}\right)_l$ and $\bar{\bar{G}}^{\times}(t')$ leads to an expression for F(t), which differs significantly from the expression found when this assumption is not made. This difference arises from the fact that the correct treatment necessarily leads to a correlation at four succeeding points of time

for a certain oscillator (e.g. the oscillator 1 in eqn.(39)). Therefore, a priori separation of IR correlation functions into two independent factors may introduce serious errors.

The same considerations are also valid for the elements of the polarizability tensor, which can be studied by Fouriertransforming Raman bandshapes (1,2). Only the isotropic part of the polarizability will not introduce correlations at four succeeding points of time. Therefore the time dependence given in eqn.(50) will be valid for the correlation function of the isotropic part of the polarizability tensor. The anisotropic components will give rise to correlations at four succeeding points of time. This means, that the vibrational correlation function involving the isotropic part of the polarizability will in general be different from the vibrational correlation function depending on the anisotropic component and from the IR vibrational correlation function. It follows that the widely used Raman method (1,2) to separate vibrational and rotational contributions is incorrect, as in this procedure it is assumed that the vibrational correlation function for the isotropic part of the polarizability tensor is equal to the IR vibrational correlation function and the vibrational correlation function of the anisotropic part of the polarizability.

It should be borne in mind that eqn.(47) is only valid if the neglect of translational diffusion is a reasonable approximation. This seems valid for CH_2Cl_2; $\tau_t = 8.5.10^{-12}$ sec.(17). At longer times modulation by translational diffusion will be important. Assuming arbitrarily an exponential decay for the translational diffusion it can easily be shown that ln F(t) then becomes

$$\ln F(t) = -A\{\tau_t\left(|t| + \tau_t(e^{-|t|/\tau_t} - 1)\right) + 2\tau_2'\left(|t| + \tau_2'(e^{-|t|/\tau_2'} - 1)\right)\} \quad (51)$$

Here τ_t is the translational correlation time and $\tau_2' = \left(\tau_2^{-1} + \tau_t^{-1}\right)^{-1}$. Eqn.(51) shows that both in the fast and slow modulation limit ln F(t) reaches the usual time dependences (7).

In the slow modulation limit ($|t| \ll \tau_2'$);

$$\ln F(t) = -{}^{3}/_{2}At^{2} \tag{52}$$

and for the fast modulation limit ($|t| \gg \tau_t$);

$$\ln F(t) = -A\{\tau_t + 2\tau_2'\}|t| \tag{53}$$

When ln F(t) is calculated, assuming an a priori separation of the correlation function into two independent factors, the fast modulation limit will be significantly different from eqn.(53). Taking into account translational diffusion it can easily be shown that ln F(t) then becomes

$$\ln F(t) = -3A\tau_1'|t| \tag{54}$$

where $\tau_1' = \left(2\tau_1^{-1} + \tau_t^{-1}\right)^{-1}$

The treatment of the influence of the transition dipole-transition dipole coupling on IR and Raman bandshapes, presented here, differs considerably from other approaches, published earlier (13,18,19). Valiev (13) and Fujiyama (18) estimate the influence of the interoscillator coupling on the halfwidth of IR and Raman absorption bands by calculating $\left(\left\langle G_{dip}^2(0)\right\rangle\right)^{\frac{1}{2}}$ (See Ch.I.2). However, this gives only an useful estimate of the contribution to the halfwidth, if the slow modulation limit can be considered. This can be shown by Fouriertransforming F(t) both in the fast and slow modulation limit; the halfwidth of the corresponding spectral densities will depend on $\left\langle G_{dip}^2(0)\right\rangle$ and $\left(\left\langle G_{dip}^2(0)\right\rangle\right)^{\frac{1}{2}}$ respectively. An expression for F(t) corresponding with eqn.(50) has been derived by Döge (19) to represent the influence of intermolecular vibrational relaxation on correlation functions obtained from Raman data.

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CHAPTER V

CONCLUDING REMARKS

In Ch.III, the experimental data obtained were discussed in terms of intermolecular vibrational relaxation. It was suggested that transition dipole-transition dipole coupling may account for the observed isotopic dilution effects. An important result with respect to previous work, is the significant temperature dependence of the intermolecular vibrational relaxation. This fact gives rise to the conclusion that the Rakov method to separate the rotational and vibrational linewidth is invalid.

The experimental results are confirmed qualitatively by the theoretical calculations, given in Ch.IV. The influence of intermolecular vibrational relaxation due to interoscillator coupling has been calculated approximately using a simplified model for the liquid. The experimental results are roughly predicted by the obtained expression for the intermolecular vibrational relaxation (Ch.IV; eqn.(47)). The theory shows the dependence of the isotopic dilution effect on the integrated absorption intensity (represented by $\left(\frac{\partial\mu}{\partial Q}\right)^4$), the temperature dependence (mainly represented by τ_2) and the linear dependence on the concentration (N in eqn.46a). Furthermore it is explicitly shown that the a priori separation of the dipole moment correlation function into independent rotational and vibrational parts yields a different time dependence.

The agreement between theory and experiment is underlined by a quantitative comparison. This is performed for some data on CH_2Cl_2. Because the experimental error on the isotopic dilution effect is relatively large for low concentrations the comparison will be

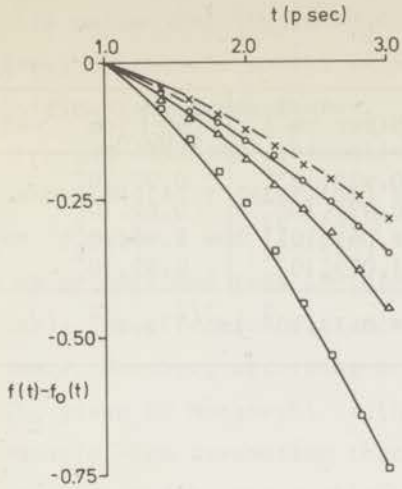

Fig.1. Comparison between theory and experiment for CH_2Cl_2 (molfr.1.0).
□: data at -90°C, Δ: -60°C
o: -20°C, ×: 30°C.
——: theoretical curves (see text).

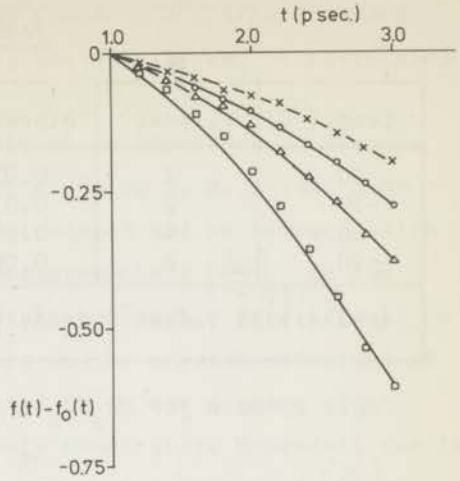

Fig.2. Comparison between theory and experiment for CH_2Cl_2 (molfr.0.84).
□: data at -90°C, Δ: -60°C
o: -20°C, ×: 30°C.
——: theoretical curves (see text).

confined to solutions with a high concentration of CH_2Cl_2 molecules (molfr. 1.0 and 0.84). For these solutions $f(t)-f_0(t)$ can be determined at different temperatures using the data, presented in Ch.III. The Fig.1-2 show for each concentration $f(t)-f_0(t)$ at different temperatures. The figures illustrate that theoretically predicted curves (according to eqn.(47) in Ch.IV) give a reasonable fit with the experimental results. It should be noted here, that the theoretical expression for $f(t)-f_0(t)$ is given by

$$f(t)-f_0(t) = \ln F(t)-\ln F(t_0) \qquad (1)$$

in which t_0 is 1 psec here. The fitting procedure has been performed by using appropriate τ_2-values as obtained from NMR-data (1) at different temperatures. These values have been listed in Table I and II.

TABLE I

temp. (^oC)	τ_2(psec)	A($psec^{-2}$)	N(per cm^3)	$\left(\frac{\partial\mu}{\partial Q}\right)$ ($cm^{3/2}sec^{-1}$)
30	1	0.039	$0.928.10^{22}$	$0.90.10^2$
-20	2	0.039	$0.991.10^{22}$	$0.89.10^2$
-60	4	0.044	$1.041.10^{22}$	$0.90.10^2$
-90	8	0.067	$1.079.10^{22}$	$0.99.10^2$
α_0=2πc.1265 $radsec^{-1}$, d=4Å, $\left(\frac{\partial\mu}{\partial Q}\right)_{IR}$ = $0.71.10^2$ $cm^{3/2}$ sec^{-1}				

Table I. Data for CH_2Cl_2 (molfr.1.0).

TABLE II

temp. (^oC)	τ_2(psec)	A($psec^{-2}$)	N(per cm^3)	$\left(\frac{\partial\mu}{\partial Q}\right)$ ($cm^{3/2}sec^{-1}$)
30	1	0.027	$0.780.10^{22}$	$0.86.10^2$
-20	2	0.031	$0.832.10^{22}$	$0.87.10^2$
-60	4	0.037	$0.874.10^{22}$	$0.90.10^2$
-90	8	0.055	$0.906.10^{22}$	$0.98.10^2$
α_0=2πc.1265 $radsec^{-1}$, d=4Å, $\left(\frac{\partial\mu}{\partial Q}\right)_{IR}$ = $0.71.10^2$ $cm^{3/2}$ sec^{-1}				

Table II. Data for CH_2Cl_2 (molfr.0.84).

In this way it is possible to estimate experimentally the quantity A, defined in eqn.(46a), which has been given in Table I and II.

It may be concluded from these data, that both theory and experiment show that $f(t)-f_0(t)$ is not linear in time and depends on the reorientational motion of the molecules as represented by τ_2. The experimental temperature dependence of the measured isotopic dilution effect is accounted for in the theoretical expression for ln F(t) by the temperature dependence of A and τ_2. The increase of A is predicted theoretically (eqn.46a) by the change of N with decreasing temperature, assuming that $\left(\frac{\partial\mu}{\partial Q}\right)$, α_0 and d are temperature independent. Especially between 30^oC and -60^oC the agreement is surprisingly good. The magnitude of N has been obtained using the

density values for liquid CH_2Cl_2 at +40°C and -100°C (2). Assuming a linear dependence on the temperature, the density can be calculated at intermediate temperatures.

To test the theoretical result it is important to discuss the experimentally determined values of A. Using N, d, α_0 and A as given in Table I and II, $\left(\frac{\partial\mu}{\partial Q}\right)$ can be calculated and be compared with the value obtained from IR-intensity measurements ($\left(\frac{\partial\mu}{\partial Q}\right)_{IR}$ in the tables). The effective distance of closest approach d is difficult to estimate. However, according to the data on the crystal structure of CH_2Cl_2 given by Marzocchi (2), the listed value for d seems reasonable. The assumption that A is only temperature dependent due to N, is confirmed by the negligible temperature dependence of $\left(\frac{\partial\mu}{\partial Q}\right)$. Furthermore the agreement between $\left(\frac{\partial\mu}{\partial Q}\right)$ and $\left(\frac{\partial\mu}{\partial Q}\right)_{IR}$ is reasonable. With N, d, α_0 and $\left(\frac{\partial\mu}{\partial Q}\right)_{IR}$ it is also possible to estimate a theoretical value for A; this results in A_{th} = 0.015 $psec^{-2}$ at 30°C for the pure liquid and A_{th} = 0.013 $psec^{-2}$ at 30°C for the solution (molfr.0.84).

Taking into account the large uncertainties in d and $\left(\frac{\partial\mu}{\partial Q}\right)_{IR}$ combined with the fact, that A depends on d^3 and $\left(\frac{\partial\mu}{\partial Q}\right)^4$ respectively, A_{th} agrees satisfactorily with the experimentally obtained values. It can be concluded that the transition dipole-transition dipole interaction accounts for the isotopic dilution effect.

With respect to this, it is important to stress, that for obtaining a reliable estimate of the importance of intermolecular vibrational relaxation it is necessary to compare an absorption band of a pure liquid with the one in infinite isotopic dilution (Both for IR and Raman bandshapes). For instance the procedure performed by Döge (3) to ascribe the whole vibrational correlation function to interoscillator interaction, can give rise to serious errors in the estimated values of interaction parameters. This is confirmed by the experimentally obtained value of $1/3 \langle(\Delta\omega)^2\rangle$ for CH_3J in Döge's paper ($1/3\langle(\Delta\omega)^2\rangle \cong A$). Taking into account the IR absorption intensity of this normal mode (resulting in a value of $\left(\frac{\partial\mu}{\partial Q}\right)_{IR}$ = $0.50.10^2 cm^{3/2}\ sec^{-1}$), the density, the frequency of the bandcentre and a realistic value for d(∿4Å), $A_{th} = 0.010.10^{24}\ sec^{-2}$.

This value of A_{th} differs dramaticly from Döge's experimental value; $A \cong 0.22.10^{24}$ sec^{-2}.

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SAMENVATTING

In dit proefschrift worden de resultaten besproken van een onderzoek naar de invloed van intermoleculaire vibratierelaxatie op de correlatiefunctie voor het vibratie overgangsdipoolmoment. Deze correlatiefuncties worden verkregen door Fouriertransformatie van IR bandvormen. Het in dit proefschrift beschreven onderzoek is verricht aan de banden van CH_2Cl_2 (1265 cm^{-1}),$CHCl_3$ (1215 cm^{-1}), $CDCl_3$ (910 cm^{-1}) en $CHBr_3$ (1142 cm^{-1}).

In deze vier gevallen is het mogelijk met behulp van de isotopenverdunningsmethode de wisselwerkingen, die de intermoleculaire vibratierelaxatie veroorzaken, te onderdrukken. De veranderingen aan de bandvorm en de correlatiefunctie ten gevolge van isotopenverdunning kunnen in goede benadering worden toegeschreven aan het verdwijnen van de intermoleculaire vibratierelaxatie.

De gemeten effecten worden verklaard door de overgangsdipool-overgangsdipoolwisselwerking tussen identieke oscillatoren in de vloeistof. Dat deze interpretatie gerechtvaardigd is wordt aangetoond door de frappant goede overeenkomst tussen de experimenteel gemeten effecten en een theoretische berekening.

Zowel experimenteel als theoretisch blijkt dat intermoleculaire vibratierelaxatie afhankelijk is van de concentratie, de geintegreerde absorptieintensiteit en het reoriëntatiegedrag van de moleculen in de vloeistof.

Aan de hand van deze resultaten zijn enkele belangrijke conclusies te trekken. Ten eerste is de gebruikelijke scheiding van de correlatiefunctie in een product van twee onafhankelijke correlatiefuncties (de rotatie- en vibratiecorrelatiefunctie) niet juist. Dit wordt aangetoond door een theoretische behandeling van overgangsdipoolmomentcorrelatiefuncties. Ten tweede is het onjuist om aan te nemen, dat vibratierelaxatie temperatuur onafhankelijk zou zijn. Dit wordt geillustreerd door de temperatuur afhankelijkheid van de gemeten isotopenverdunningseffecten. Deze temperatuur afhankelijkheid van de

intermoleculaire vibratierelaxatie kan vrijwel geheel worden toegeschreven aan de invloed van de moleculaire reoriëntatie op de vibratierelaxatie.

Op verzoek van de Faculteit der Wiskunde en Natuurwetenschappen volgt hier een kort overzicht van mijn academische studie.

Na het behalen van het einddiploma HBS-B aan het Pauluslyceum te Tilburg in juli 1964, begon ik in oktober van hetzelfde jaar met de studie in de scheikunde aan de Rijksuniversiteit te Leiden. Het kandidaatsexamen, letter G, werd in mei 1967 afgelegd. De doctoraal studie, met als hoofdvak fysische chemie, bijvak theoretische natuurkunde en als derde richting organische chemie, vond plaats onder leiding van de hoogleraren Dr. M.Mandel, Dr. P.Mazur, Dr.P.W.Kasteleyn en Dr. E.Havinga. Het doctoraal examen werd in januari 1970 afgelegd.

Hierna werd het in dit proefschrift beschreven onderzoek begonnen. Vanaf 1 februari 1970 was ik als doctoraal assistent verbonden aan de afdeling fysische chemie. Met ingang van 1 oktober 1973 werd ik benoemd tot wetenschappelijk medewerker.

Gaarne wil ik op deze plaats mijn dank betuigen aan allen, die hebben medegewerkt aan het tot stand komen van dit proefschrift. In het bijzonder gaat mijn dank uit naar mijn ouders, die het mij mogelijk gemaakt hebben, een academische studie te volgen. De stimulerende discussies met mijn promotor Dr. J.C.Leyte en Drs.J.de Bleijser wil ik gaarne vermelden. De heren Drs.P.M.J.Burgers en M.de Zwart hebben in het kader van hun doctoraal studie belangrijke bijdragen aan het onderzoek geleverd. De tekeningen werden verzorgd door de heren M.Pison, J.J.Pot en A.G.Huigen. Het typen van het manuscript werd verricht door mijn vrouw.