MOLECULAR INTERACTION-INDUCED CONTRIBUTIONS TO RAYLEIGH AND RAMAN LIGHT SCATTERING [*]

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I. THE SOURCES OF SCATTERED RADIATION

In their fundamental papers, of undiminished validity to the present day, Einstein [1] and Smoluchowski [2] have shown that the cause of light scattering resides in fluctuations of the medium due primarily to thermal motions of the molecules and modifying the over-all optical properties, especially if molecular interactions are perceptibly present [3,4]. The light scattered with frequency ω and wave vector $\vec{k}$ is proportional to the fluctuating source term, defined as [3] :

$$\delta\vec{S}(\vec{k},\omega) = \delta\vec{P}(\vec{k},\omega) - \left(\frac{\langle\varepsilon\rangle-1}{4\pi}\right)\delta\vec{E}(\vec{k},\omega) , \qquad /1/$$

where $\delta\vec{P}$ is the total fluctuating polarization, $\delta\vec{E}$ the fluctuating Maxwell field, and $\langle\varepsilon\rangle$ the average dielectric constant of the medium. Since the equilibrium average of the source function defined as

$$\vec{S} = \vec{P} - \frac{\langle\varepsilon\rangle-1}{4\pi}\vec{E} \qquad /2/$$

is zero: $\langle\vec{S}\rangle = 0$ /the fluctuations $\delta\vec{S}$ occur about a mean value which is zero/, the evolution in time of the scattered intensity can be expressed by way of the auto-correlation function of $\vec{S}$ [5] :

$$I_\gamma(\vec{k},t) = \left\langle S_\gamma(-\vec{k},0)\ S_\gamma(\vec{k},t)\right\rangle \qquad /3/$$

The source function can be expressed in terms of the tensor of dipolar collective polarizability of the medium $\underline{\underline{\Pi}}$ [3-7]:

$$\vec{S} = \left(\frac{n^2 + 2}{3}\right)^2 \underline{\underline{\Pi}} \cdot \langle \vec{E} \rangle \qquad /4/$$

where $\langle \vec{E} \rangle$ is the averaged Maxwell field existing in the scattering medium. The total dipole moment $\vec{M}$ of a system can be calculated from the formula $[3\text{-}7]$

$$\vec{M} = \sum_{i=1}^{N} {}_{(i)}\underline{\underline{A}} \cdot \vec{E}_0 + \sum_{i=1}^{N} \sum_{j\neq i} {}_{(i)}\underline{\underline{A}} \cdot \underline{\underline{T}}^{(ij)} \cdot {}_{(j)}\vec{\mu} \quad , \quad /5/$$

where $\underline{\underline{T}}^{(ij)}$ is the dipole interaction tensor, $_{(j)}\vec{\mu}$ the dipole moment of a j-th molecule and $\vec{E}_0$ the incident electric field. Its iterative solution for the collective polarizability can be put in the form of the following sum:

$$\underline{\underline{\Pi}} = {}^{(0)}\underline{\underline{\Pi}} + {}^{(1)}\underline{\underline{\Pi}} + {}^{(2)}\underline{\underline{\Pi}} + \ldots = {}^{(0)}\underline{\underline{\Pi}} + \Delta\underline{\underline{\Pi}} \quad , \quad /5a/$$

where the superscripts (n) to the left of $^{(n)}\underline{\underline{\Pi}}$ symbolize the order of approximation of the successive contributions to $\underline{\underline{\Pi}}$. The solution $^{(0)}\underline{\underline{\Pi}}$ in the zeroth approximation is given by the sum of intrinsic polarizabilities of the molecules, regarded as not interacting with one another,

$$^{(0)}\underline{\underline{\Pi}} = \sum_{i=1}^{N} {}_{(i)}\underline{\underline{A}} \qquad /6/$$

and is the tensor of collective polarizability of the medium in the absence of molecular interactions. Since, here, we consider light scattering in the dipolar approximation, the tensor $\underline{\underline{\Pi}}$ of collective polarizability of the medium is a dipole polarizability tensor. Owing to interactions between the molecules, however, multipolar /dipole-multipole/ mechanisms too have something to contribute to $\underline{\underline{\Pi}}$. Thus, quite

generally, this mechanism /involving dipoles induced by
multipoles/ giving rise to polarizability can be referred
to as dipole-induced multipole polarizability. We shall now
write down the respective general formulae determining the
first two contributions $^{(1)}\mathcal{K}$ and $^{(2)}\mathcal{K}$ to the dipolar
collective polarizability of the system due to different
multipolar mechanisms $[7]$ /with dipolar mechanisms as a
particular case, when m=n=1 in /7a/ ; m=n=s=u=1 in /7b/

$$^{(1)}\underline{\underline{\mathcal{K}}} = \sum_{i=1}^{N} \sum_{j\neq i} \sum_{m,n=1}^{\infty} C_{mn} \,_{(i)}\underline{\underline{A}}^{(1)(m)}_{[m]} \,^{(m)}\underline{\underline{G}}^{(n)}_{ij} \,_{[n]} \,_{(j)}\underline{\underline{A}}^{(n)(1)} \qquad , \qquad /7a/$$

$$^{(2)}\underline{\underline{\mathcal{K}}} = \sum_{i=1}^{N} \sum_{j\neq i} \sum_{k\neq j} \sum_{m,n,s,u} (-)^{m+u} C_{mnsu} \,_{(i)}\underline{\underline{A}}^{(1)(m)}_{[m]} \,^{(m)}\underline{\underline{G}}^{(n)}_{ij}$$

$$_{[n]} \,_{(j)}\underline{\underline{A}}^{(n)(s)}_{[s]} \,^{(s)}\underline{\underline{G}}^{(u)}_{jk} \,_{[u]} \,_{(k)}\underline{\underline{A}}^{(u)(1)} \qquad\qquad /7b/$$

where

$$C_{m\ldots u} = \left[(2m-1)!! \ldots (2u-1)!! \right]^{-1} \quad ,$$

and $^{(n)}G^{(s)}_{pq}$ denotes the 2^n-pole —— 2^s pole dynamic propaga-
tor between the molecules p and q.

The further treatment of the mathematics of the scatte-
red light intensity depends on the physics of the system un-
der consideration. If the fluctuations in orientation of the
molecules /described by $^{(o)}\mathcal{K}^{(2)}$/ decay much more slowly than
the interaction-induced part $\Delta\underline{\mathcal{K}}^{(2)}$ of the collective pola-
rizability /as it is the case e.g. in CS_2/, it becomes
possible to separate the orientational part of the experi-
mentally observed scattered spectrum; in this case we deal
with what is referred to as the description of the scatte-
ring process in projection scheme because we are able to

separate the Fourier component inherent in $\Delta \Im^{(2)}(t)$ of fluctuations corresponding to reorientational motions of the molecules by having recourse to projection operator method [8-10].

The collective polarizability responsible for scattering due to fluctuations in orientation now takes the following form:

$$^{(OF)}\Im_{\alpha}^{(2)}(t) = \left(1 + \frac{\langle \Delta\Im^{(2)} \odot {}^{(0)}\Im^{(2)}\rangle}{\langle {}^{(0)}\Im^{(2)} \odot {}^{(0)}\Im^{(2)}\rangle}\right) {}^{(0)}\Im_{\alpha}^{(2)}(t), \quad /8/$$

whereas the remaining part

$$^{(PI)}\Im_{\alpha}^{(2)}(t) = \Im_{\alpha}^{(2)}(t) - \frac{\langle \Delta\Im^{(2)} \odot {}^{(0)}\Im^{(2)}\rangle}{\langle {}^{(0)}\Im^{(2)} \odot {}^{(0)}\Im^{(2)}\rangle} \, {}^{(0)}\Im_{\alpha}^{(2)}(t) \quad /9/$$

is referred to as the purely interaction-induced source of scattered radiation. With a view to our further calculations it is preferable to introduce the notation of spherical tensors. We thus have

$$^{(0)}\Im_{\alpha}^{(2)} = \sqrt{\frac{2}{3}} \, \gamma \sum_{i=1}^{N} D_{\alpha 0}^{(2)*}(\hat{\vec{u}}) = \gamma \sum_{i=1}^{N} \left(\hat{\vec{u}}\hat{\vec{u}} - \frac{I}{3}\right)_{\alpha}^{(2)}, \quad /10/$$

where $\gamma = a_{\parallel} - a_{\perp}$ is the intrinsic anisotropy of the molecule. If there is no separation in time between the orientational fluctuations and interaction-induced mechanisms, we are unable to decompose the spectral line of scattered radiation observed in experiment into its orientational part and its interactionally induced part. Interferences between the two mechanisms then lead to the emergence of a significant cross contribution, negligible in the preceding case of time-separation. The most natural

description for the scattered radiation intensity in the
present case is that of the non-projection scheme /without
projection operator/ [11] . Mathematically, prior to the
calculation of the intensity /3/, the polarizability $\mathfrak{X}$ of
Eq. /5/ is subject to no further transformations, though
obviously the comparison of the results analytically obtai-
ned within the framework of this description and those ob-
tained in experiment is much more difficult. Recently, com-
puter simulations experiments   by the method of molecular
dynamics (MD) [11-15] are made use of when studying various
aspects of light scattering /beside experiments in the labo-
ratory/. Such simulations can be performed within either of
the above described scattering schemes. Hence it is highly
useful to be able to switch from the projection scheme to
the non-projection scheme, and vice versa.

II. LIGHT SCATTERING, DESCRIBED WITHIN THE NON-PROJECTION
     SCHEME. NUMERICAL CALCULATIONS OF THE INTEGRAL INTEN-
     SITY FOR SOME SELECTED MOLECULES.

     On assuming permutational symmetry of the collective
polarizability tensor of the medium $\mathfrak{X}_{\mu\rho} = \mathfrak{X}_{\rho\mu}$ it is
possible to distinguish two qualitatively different parts
of the scattered intensity /3/: an isotropic part /l=0/,
and an anisotropic part /l=2/ [16]:

$$I_{\vec{\pi}}\left(\vec{k},t\right) \cdot \sum_{l=0,2} I_{\vec{\pi}}^{(l)}\left(\vec{k},t\right) \qquad /11/$$

either of which can be written down in the form of the
product

$$I_{\vec{\varkappa}}^{(\ell)}(\vec{k},t) = A_\omega \, \phi_{\ell\ell} \, F_{\ell\ell}(\vec{k},t) \qquad /12/$$

of a molecular factor

$$F_{\ell\ell}(\vec{k},t) = \left\langle \underline{\underline{\mathfrak{X}}}^{(\ell)}(-\vec{k},0) \odot \underline{\underline{\mathfrak{X}}}(\vec{k},t) \right\rangle , \qquad /12a/$$

a geometrical factor /in the case of linearly polarized light/

$$\phi_{00} = \frac{1}{3}\left(\vec{e}\cdot\vec{\varkappa}\right)^2 , \qquad \phi_{\varkappa\varkappa} = \frac{\left(\vec{e}\cdot\vec{\varkappa}\right)^2 + 3}{30} , \qquad /12b/$$

and a factor dependent on the macroscopic properties of the scattering medium and those of the incident radiation

$$A_\omega = \left(\frac{n_{\omega_i}^2 + 2}{3}\right)^2 \left(\frac{n_{\omega_s}^2 + 2}{3}\right)^2 \left(\frac{I_0}{R^2}\right)\left(\frac{\omega_s}{c}\right)^4 . \qquad /12c/$$

When considering the scattered radiation intensity in the scheme without projection operator, the collective polarizability of Eq. /12a/ is simply given by the sum /5/. We now have

$$F_{\ell\ell}(\vec{k},t) = \sum_{a,b=0,1,2\ldots} {}^{(ab)}F_{\ell\ell}(\vec{k},t) , \qquad /13/$$

with

$$^{(ab)}F_{\ell\ell}(\vec{k},t) = \left\langle {}^{(a)}\underline{\underline{\mathfrak{X}}}^{(\ell)}(-\vec{k},0) \odot {}^{(b)}\underline{\underline{\mathfrak{X}}}^{(\ell)}(\vec{k},t) \right\rangle, \quad /14/$$

where $\odot$ denotes tensor scalar product.

Each of the successive terms of Eq. /5a/ contributes to the scattered intensity. Generally, cross terms also appear owing to interference between the two mechanisms underlying Eq. /5a/. If the decay times of the fluctuations of the individual terms of /5a/ are comparable /if decay proceeds on the same time scale/, it is very difficult or even impossible to separate the individual contributions in laboratory experiments /this is essentially the case when dealing with light molecules like N_2, O_2/. In computer experiments, however, we are able to calculate the various contributions individually; thus, it appears desirable to discuss them separately. In laboratory experiments we are compelled to analyze their sum —— the total scattered intensity.

In what follows, we shall not be dealing with the fine structure of the scattered spectrum and so are justified in putting $\vec{k} = 0$ in the formulae for the scattered intensity. Moreover, we shall restrict our considerations to the aniso-tropic part of the scattered radiation, thus putting l=2.

Here, we shall consider the integral intensity; in Section 4, we shall deal with its spectral distribution /its decay time/.

In order to calculate the individual parts by analytical methods one has to express the collective polarizability of the medium in the language of spherical tensors. This has been performed by us in the first and second approximations of the DID model [11] and, lately, in the approximation of an arbitrary dipole-multipole mechanism [17,18]. This language enables one to make use of the results of computer simulations [19,20] for the spherical components

$\varepsilon_{11}\,'_m \left(r_{12} \right)$ of the binary distribution function /henceforth we shall be considering linear molecules/ [21]

$$g^{(2)}\left(r_{12}, \underline{\Omega}_1^{12}, \underline{\Omega}_2^{12} \right) = 4\pi \sum_{\ell\ell'm} g_{\ell\ell'm}(r_{12})\, Y_m^\ell(\underline{\Omega}_1^{12})\, Y_m^\ell(\underline{\Omega}_2^{12}) \quad /15/$$

which suffices for carrying out most of averings occurring in the respective expressions. Our calculations shall concern liquid N_2 and shall be performed for two mechanisms of interactional induction of collective polarizability: /i/ dipole-induced dipole /DID/, and /ii/ dipole-induced octupole /DIO/, as well as liquid O_2 for the DID mechanism only /since numerical data for the dipole-octupole polarizability tensor components of O_2 are lacking/. The omission of the quadrupole mechanism in $^{(1)}\underline{\underline{\pi}}$ in our computations is due to the presence of a centre of symmetry in N_2 and O_2 /$A_{\alpha\beta\gamma}=0$/. Since those two molecules fail to present time-scale separation, we shall adopt the non-projection scheme. An essential, difficult problem in calculations of this kind resides in the necessity of taking into account analytically and numerically the radial and angular-radial correlations of higher orders. The procedure with regard to the ternary and quaternary radial correlations has been described i.a. in our previous paper [11]. Here, we shall moreover take into consideration the ternary angular-radial correlations applying the approximation of Ladanyi and Keyes [22]:

$$\left\langle \underline{\underline{\pi}}(ij) \odot \underline{\underline{\pi}}(ik) \right\rangle_{g^{(3)}(\vec{R}_i,\vec{R}_j,\vec{R}_k)} = \left\langle \underline{\underline{\pi}}(ij) \odot \underline{\underline{\pi}}(ik) \right\rangle_{h(\vec{R}_i,\vec{R}_j)h(\vec{R}_i,\vec{R}_k)} \quad /16/$$

rejecting, as negligible, the "irreducible connected terms". As shown by the computer results of Frenkel and Mc Tague

[12] and Ladanyi [23,24], this approximation tends to ove-
restimate somewhat the absolute value of the angular-radial
three-body terms, although the sign and the order of the
magnitude are correctly predicted. The values of the inte-
gral intensity for the individual parts of the radiation
scattered by liquid N_2 and O_2 are given in Table I.

Among the interaction-induced contributions to the
integral intensity, noteworthy is the high value of the
cross term $^{(10+01)}F_{22}$ in both N_2 and O_2. $^{(11)}F_{22}(S)$ is the
quadratic term, calculated in the approximation of binary,
ternary and quaternary radial correlations; more precisely,
it is calculated within the approximation of the S-model
[25-27]   which assumes the molecules of a system to be
correlated radially but not angularly. The term $^{(11)}F_{22}(3AR)$
accounts for the ternary angular-radial correlations within
the approximation discussed above /Eq.16/. Interesting is
the considerable mutual cancelling of the negative term
$^{(11)}F_{22}(2AR)$/binary angular-radial correlations/ and the po-
sitive term $^{(11)}F_{22}(3AR)$. This mutual reduction is found both
for N_2 and O_2. It is our opinion that this cancelling acco-
unts for the excellent applicability /discussed by De Santis,
Sampoli and Vallauri [15]/of the S-model to the description
of the total intensity of the quadratic part $^{(11)}F_{22}$ of the
scattered radiation. Since there are no values of the octupo-
le polarizability components for molecules other than N_2 we
were unable to calculate these multipolar contributions for
O_2.

As we notice from Table I, the over-all contribution for N_2
resulting from the dipole-induced octupole and quadrupole-
-quadrupole mechanisms amounts to $0.076 * 10^{-1}A^6$, which
makes 3.1 per cent of the total intensity. This DIO contri-
bution is positive in contradistinction to the over-all con-
tribution from the dipole-induced dipole mechanism. The di-
pole-induced octupole is responsible for the rise in scat-
tered intensity compared to its rather drastic decrease due
to changes caused by the first order approximation of the

Table I. Values for the individual terms of the molecular part $^{(ab)}F_{22}$ of the integral intensity /per one molecule/ of light Rayleigh scattered by liquid nitrogen and oxygen. The true values are multiplied by a factor of 10.

Approximation	Term	Molecule	
		N_2^{*}	O_2^{**}
M	$^{(00)}F_{22}$	3.478	8.13
DID	$^{(10+01)}F_{22}$	−1.257	−3.25
	$^{(11)}F_{22}^{(S)}$	0.137	0.191
	$^{(11)}F_{22}^{(2AR)}$	−0.118	−0.319
	$^{(11)}F_{22}^{(3AR)}$	0.129	0.293
	$^{(20+02)}F_{22}$	0.010	0.016
DIO	$^{(10+01)}F_{22}$	0.081	-
	$^{(11)}F_{22}^{(S)}$	0.006	-
	$^{(11)}F_{22}^{(2AR)}$	−0.085	-
	$^{(11)}F_{22}^{3AR}$	0.060	-
DIO + QIQ	$^{(20+02)}F_{22}$	0.014	-

*,** Thermodynamical states

N_2 S^{*} = 0.659, T^{*} = 1.79

O_2 S^{*} = 0.50, T^{*} = 1.54

DID model. Ladanyi [28] computed the changes due to higher order terms in DID interactions on the depolarized light scattering intensity in liquid oxygen, finding that the higher than first-order contributions to polarizability also give a positive /by contrast to the first-order/ contribution. Ladanyi estimated them at 2.8 per cent of the total scattered light. We previously calculated very similar changes for N_2 [11]. The changes due to the DIO mechanism reported here are of the same order of magnitude.

The light scattered intensity due to multipolar mechanisms in fluids of simple molecules, though not great quantitatively, entails an important consequence with regard to the spectral description of the scattered radiation. We immediately note that the dipole-octupole scattering mechanism is responsibile for rotational transitions governed by the following selection rules: $\Delta J_1 = 0, \pm 2$; $\Delta J_2 = \pm 2, \pm 4$. Then a substantial part of the octupolar intensity is located on the far wings of the spectral line. Moreover, multipolar mechanisms strongly influence the spectral distribution of the isotropic part $F_{00}(\omega)$ of the scattered radiation. Careful spectral measurements [29,30] indicate a substantial decrease in the depolarization ratio at the wings of the spectral line. That behaviour of the frequency-dependence of the depolarization ratio in N_2 and O_2 cannot be explained within the DID model [29,30]. Assuming approximately that the overall intensity due to octupole mechanism is located at the wings, we calculate the depolarization ratio of the wings as:

$$\eta(\omega_{wing}) = \left[\frac{4}{3} + \frac{I_{VV}^{iso}}{I_{VH}^{aniso}} \right]^{-1} \qquad /17/$$

where the polarized isotropic I_{VV}^{iso} as well as depolarized anisotropic I_{VH}^{aniso} parts of scattered radiation are due to the DIO mechanism.

Performing numerical calculations for N_2 we get
$\eta(\omega_{wing}) = 0.69$. The DID model leads to $\eta(\omega_{wing}) = 0.74$.
For N_2 Raman scattering we get $\eta(\omega_{wing}) = 0.47$.

III. DESCRIPTION OF LIGHT SCATTERING IN PROJECTION SCHEME

In many a case, however, decay of the fluctuations in orientation proceeds much more slowly than that of the fluctuations of the mechanisms induced by interactions. The collective polarizability of the system related with fluctuations of orientation is given by the expression /8/. The latter gains in clarity if one has recourse to the concept of effective molecular anisotropy $\gamma_{eff} = \gamma + \Delta\gamma$. Eq. /8/ becomes

$$^{(OR)}\mathcal{X}_\alpha^{(2)} = \gamma_{eff} \sum_{i=1}^{N} \left(\hat{\vec{u}}_{(i)} \hat{\vec{u}}_{(i)} - \frac{\underline{\underline{I}}}{3} \right)_\alpha^{(2)} . \qquad /18/$$

Clearly, the time-dependence of $^{(OR)}\mathcal{X}_\alpha^{(2)}$ is identical with the time-dependence of the anisotropic part of the unperturbed polarizability /10/. Now, Eq. /18/ involves part of the interaction induced mechanisms, since

$$\frac{\Delta\gamma}{\gamma} = \frac{\left\langle \Delta\mathcal{X}^{(2)} \odot {}^{(0)}\mathcal{X}^{(2)} \right\rangle}{\left\langle {}^{(0)}\mathcal{X}^{(2)} \odot {}^{(0)}\mathcal{X}^{(2)} \right\rangle} \qquad /19/$$

Keyes and Ladanyi [22] have shown how Eq. /18/ can be derived from fundamental considerations concerning anisotropic fluctuations in a scattering medium having recourse to the theory of linear response. The purely interaction-induced part /9/ of the collective polarizability can now be written as follows:

$$(\text{PII}) \; \mathcal{N}_\alpha^{(2)} = \Delta \mathcal{N}_\alpha^{(2)} - \Delta \gamma \sum_{i=1}^{N} \left({}_{(i)}\vec{u}\, {}_{(i)}\vec{u} - \frac{\mathbf{I}}{3} \right)_\alpha^{(2)} \qquad /20/$$

Within this scheme, already referred to as the projection
scheme description, we again are able to distinguish three
parts of the scattered intensity: /i/ a part due to orien-
tational fluctuations which originates in Eq. /18/, /ii/ a
purely interaction-induced part, resulting from /20/, and
/iii/ a cross part representing interference of the mecha-
nisms /18/ and /20/. All three parts are readily expressed
using the above introduced molecular factors $^{(ab)}F_{22}(t)$,
Eq. /14 /. This procedure enables us to go over with ease
from the description of the intensity in non-projection
scheme to its description in projection scheme, and vice
versa. In fact, we have [16]:

$$(\text{OF}) \; I_{\vec{n}}^{(\ell=2)}(t) = G \left(\frac{\gamma_{\text{eff}}}{\gamma} \right)^{2} {}^{(00)}F_{22}(t) \qquad , \qquad /21a/$$

$$(\text{PII}) \; I_{\vec{n}}^{(\ell=2)}(t) = G \left[{}^{(11)}F_{22}(t) - 2 \frac{\Delta\gamma}{\gamma} {}^{(10)}F_{22}(t) + \left(\frac{\Delta\gamma}{\gamma} \right)^{2} {}^{(00)}F_{22}(t) \right], \qquad /21b/$$

$$(\text{cross}) \; I_{\vec{n}}^{(\ell=2)}(t) = G \, 2 \, \frac{\gamma_{\text{eff}}}{\gamma} \left[{}^{(10)}F_{22}(t) - \frac{\Delta\gamma}{\gamma} {}^{(00)}F_{22}(t) \right], \qquad /21c/$$

with

$$G = A_\omega \left[\frac{(\vec{e}\cdot\vec{n})^2 + 3}{30} \right] \qquad . \qquad /21d/$$

Obviously, analyzing the expressions /12a/ and /13/, with the time-evolution of the molecular factors $^{(00)}F_{22}(t)$, $^{(10)}F_{22}(t)$ and $^{(11)}F_{22}(t)$ available, we are able to determine the decay in time of the light intensity in the non--projection scheme description:

$$I_{n}^{(\ell=2)}(t) = G\left[^{(00)}F_{22}(t) + 2\,^{(10)}F_{22}(t) + ^{(11)}F_{22}(t)\right] \quad /22/$$

IV. TIME-DECAY OF THE SCATTERED RADIATION INTENSITY.

Analytical analyses of the time-evolution of the molecular factors $^{(00)}F_{22}(t)$, $^{(10)}F_{22}(t)$ and $^{(11)}F_{22}(t)$ are beset with enormous difficulties. The factors are determed by conditional rotational and translational motion of one, two, three and four molecules. At present, owing to developments in computer simulation methods [12-15], each of them can be analyzed individually with a high degree of accuracy. We are strongly convinced, however, that computer calculations alone are insufficient. On the basis of information gleaned numerically for selected molecules and thermodynamical states, more general analytical theories have yet to be constructed. Here, we shall discuss the short-time behaviour of the molecular factors $^{(ab)}F_{22}(t)$. It is well known that information on the short-time behaviour of the correlation function $^{(ab)}F_{22}(t)$ can be derived from its second spectral moment

$$F(t) = F(0) - \ddot{F}\Big|_{t=0}\frac{t^2}{2} + \ldots \quad /23/$$

The spectral moments of the above three correlation func-
tions /molecular factors $^{(00)}F_{22}(t)$, $^{(10)}F_{22}(t)$ and $^{(11)}F_{22}(t)$
are easy to calculate [31,32]. The resulting correlation
functions are shown in Figs 3 and 4. We shall not discuss
$^{(00)}F_{22}(t)$ here; it has been dealt with extensively e.g. in
Ref.[33]. It is our aim to consider the $F_{22}(t)$ resulting
from Eq. /23/ in relation to certain models of conditional
rotational motion of molecules. One immediately notes that
$^{(10)}F_{22}(t)$ is determined by the averaged conditional rota-
tional motion of a molecule [16] in the field of forces of
two other molecules, whose translational and rotational
coordinates are well determined /Fig.1/. Similarly, $^{(11)}F_{22}^{0}(t)$
is determined by the averaged conditional motion of two mole-
cules provided that the translational and rotational coordi-
nates of two molecules /the same, or others/ are well deter-
mined. With regard to the fact that the vibrational coordina-
tes of two molecules are mutually uncorrelated in Raman
scattering, the picture of conditional motion is simpler
than in Rayleigh scattering /the possible correlations in
the medium are fewer/. Figs 1 and 2 show schematically the
sources of the time-dependence of the molecular factors
$^{(10)}F_{22}(t)$ and $^{(11)}F_{22}(t)$ for the case of Raman scattering.

It is tempting to construct a sort of model of the
motions underlying the interaction-induced correlation
function $^{(11)}F_{22}(t)$. For short times, the motions shown in
Fig.2 can be said to be free. Earlier considerations [34,35]
prove that, here, the essential role belongs to translatio-
nal motion. On the assumption of free motion the function
$^{(11)}F_{22}(t)$, normalized to its initial value, takes the follo-
wing form:

$$^{(11)}\hat{F}_{22}(t) - d^{-3}\left[6\bar{x}^{1/2} - 18\sqrt{\frac{k_BT}{m}}\frac{t}{d} + 12\left(\frac{k_BT}{m}\right)^{3/2}\left(\frac{t}{d}\right)^3\right] \quad /24/$$

$$- g\left(\frac{k_B T}{m}\right)^{5/2}\left(\frac{t}{d}\right)^5 \; e^{-\frac{m}{k_B T}\left(\frac{t}{t}\right)^2}\Bigg] \; .$$

Above, d is the parameter of closest approach of the molecu-
les of the fluid, m the molecular mass, T the temperature,
and k_B Boltzmann's constant. The procedure leading to
Eq. /24/ resembles that applied by Ladd, Litovitz and
Montrose [36] in their analysis of $^{(11)}F_{22}(t)$ within the long-
-time diffusional approximation. The correlation function
/24/, normalized to unity at t=0, is shown for N_2 in the
upper part of the graph 3 and for CO_2 in the upper part of 4.
The lower parts of the graphs represent the short-time evolu-
tion of the cross correlation functions $^{(10)}F_{22}(t)$ for N_2 and
CO_2 respectively as derived from their second spectral mo-
ments. Finally, to gain insight into the conditional rotatio-
nal motion of the molecule /Fig.1/, we shall discuss the
short-time behaviour of the cross correlation function in
projection scheme for Raman scattering:

$$^{(CROSS)}\hat{\overset{\uparrow}{\underset{RAM}{\Big\downarrow}}}{}^{(\ell=2)}(t) = 2\,\frac{\gamma'_{eff}}{\gamma'}\left[^{(10)}F_{22}(t) - \frac{\Delta\gamma'}{\gamma'}{}^{(00)}F_{22}(t)\right] \quad /25/ .$$

It might be presumed that the conditional rotational motion
shown in Fig.1 for short times could also be approximated by
free motion. This, however, is not the case [16] . It
will be remembered that the one-molecule correlation function
$^{(00)}F_{22}(t)$ for light molecules is, for short times, well
approximable by the free rotator function. Obviously, if
$^{(10)}F_{22}(t)$ too is described by free rotator motion, the ex-
pression /25/ vanishes. Now computer simulation results show
that it does not. Thus, the correlation function describing
the conditional rotational motion of N_2 and CO_2 ---- even for
short times ----- vanishes more slowly than it would on the
assumption of free rotator motion. The correlation function
/25/ is plotted in the lower parts of graphs 3 and 4 for N_2
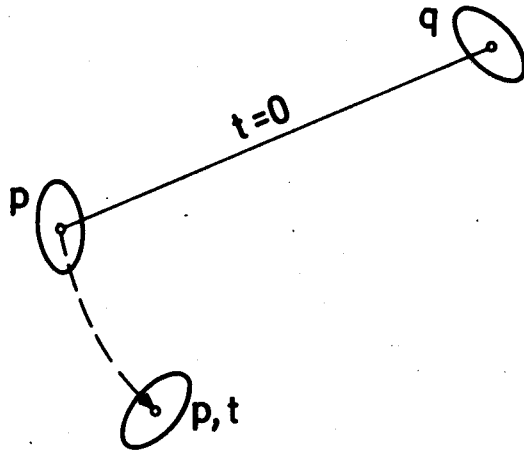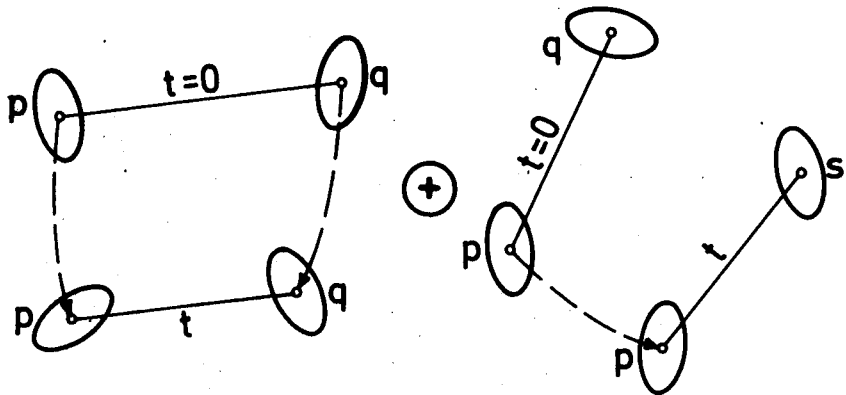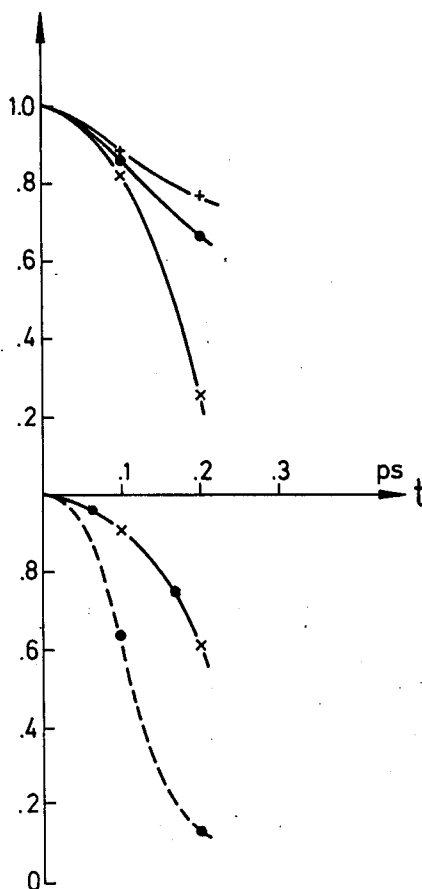and CO_2 respectively.

Fig.1.

Fig.2.

Fig.3. Short-time behaviour of the interaction-induced corre-
lation function $^{(11)}F_{22}(t)$ /upper graph/ and cross
correlation function $^{(10)}F_{22}(t)$ /lower graph/ for N_2
at $q = 0.04 Å^{-1}, T = 153° K$. —×— their behaviour calculated with
the second moments, ——+—— calculated on the above
discussed model of free translational motion of the
molecule in the fluid, ——●—— curve plotted on the
basis of computer simulation results [45] . More-
over, —————— represents the cross-correlation
function /25/ in projection scheme [45,46]   with
$^{(00)}F_{22}(t)$ calculated in the approximation of free ro-
tational motion. To economize space, the graph has
been shifted to the value 1. In reality, it begins at
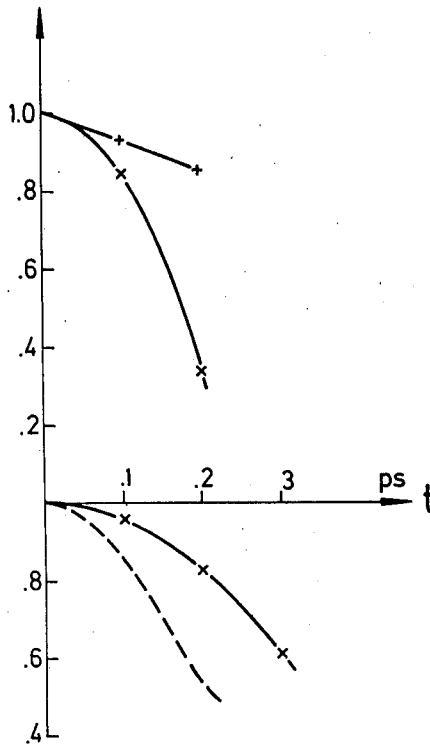zero. The selected points /full dots●/ give computer
simulation results.

Fig.4.   Short-time behaviour of the interaction-induced
         correlation function $^{(11)}F_{22}^{0}(t)$ /upper graph/ and
         cross correlation function $^{(10)}F_{22}^{0}(t)$ /lower graph/
         for CO_2 at $\mathcal{S} = 0.044\text{Å}^{-3}$, $T = 263\text{K}$. The notation is that of Fig.3.

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