

INDUCED SPECTRA IN DENSE FLUIDS: FAR INFRARED SPECTROSCOPIC CONTRIBUTIONS
TO THE UNDERSTANDING OF MOLECULAR DYNAMICS IN DENSE FLUIDS

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There is surprisingly little experimental material that can be used to test models of the molecular dynamics of dense fluids outside the hydrodynamic region. It may be that this is one of the reasons that the development of such models has made new progress only after the introduction of computer calculations on Molecular Dynamics. The short time part of the dynamics of dense fluid systems ranges from 10^{-10} - 10^{-13} sec or alternatively, from $1 - 300 \text{ cm}^{-1}$. This frequency range is the far infrared. "Induced" far infrared spectra, i.e. spectra with absorption at frequencies different from the frequencies at which the free molecules absorb must therefore be one of the most suitable sources of information about short time molecular dynamics of dense fluids.

When one examines the results in this field, one immediately surmises the difficulties. Although there has been reported on far infrared spectra of all sorts of liquids, organic solvents, mixtures and solutions, of late the systems under study become simpler. The extraction of all the information about the dynamics of the system which lies hidden in the total appearance of the absorption band is only possible with the aid of a complete and very detailed model which connects the intermolecular potential and the molecular distributions both, to the observables. Moreover, to test such models in a more quantitative way, one needs absorption measurements at different densities, temperatures and, most impossible, a continuously variable intermolecular potential.

The simple systems that have been reported on and which are suited for a quantitative theoretical approach have all in common that impurities are used as a probe. It is well known in solid state spectroscopy that impurity spectra very often give much more information about the host crystal than about the impurity. The same holds in the gaseous and liquid state. Briefly one can state that the impurity present in very low concentrations, takes part in the modes of the entire system, without disturbing these modes to any appreciable extent. Absorption intensity may, however, be induced by the impurity into modes that are inactive in the pure solvent.

Examples are ionic impurities in ionic compounds where, with the proper ratio of masses of impurity and replaced ion, in some cases the entire acoustic spectrum $f(\omega)$ with all the van Hove singularities has been observed.

Dilute solutions of He and Ne in argon [1,2] have much the same effect. The collision induced dipoles induce absorption activity into otherwise inactive modes. In solutions of N_2 and CH_4 in argon [3] it are the transitions of the quadrupole and octupole induced dipoles that are modulated by the frequency distribution of the liquid. In solutions of HCl in SF_6 [4], CCl_4 , hydrocarbons [5], argon, krypton and xenon [6,7] it are the transitions of the permanent dipoles with a comparatively very small induced dipole. In solutions of CO in argon, krypton, xenon, O_2 , CH_4 and N_2 [8], induced and permanent dipoles both play a role and these systems are therefore more difficult to interpret.

The position of the frequency of the probe transition with respect to the frequencies of the system plays a very important role. When the probe frequency is high, one can speak of an adiabatic perturbation, in terms of particles, of a Lorentz gas. Very little information is gained about the frequencies of the system. When the probe frequency is low the distribution of frequencies gives rise to a fast fluctuating random force and a Debye behaviour of the rotator or a Brownian movement of a heavy particle results. It is when the probe frequency lies right in the middle of the frequency distribution that most information is obtained.

Rotators with widely spaced transition frequencies have the advantage that one probes simultaneously different parts of the frequency spectrum of the solvent. The hydrogen halides are exceptional in this respect that the transitions from levels that are highly populated at the temperatures of interest cover the entire frequency spectrum of the fluid. By pure chance these favourable theoretical state of affairs goes together with very favourable conditions from an experimental point of view. It is therefore not surprising that these systems have attracted a lot of attention. Solutions of HCl and DCl have been studied in liquids such as CCl_4 and cyclohexane, SF_6 , argon, krypton and xenon. A brief inspection of the different appearances of these spectra shows that the remainder of the rotational fine structure becomes more pronounced in the order CCl_4 , argon, krypton, xenon, SF_6 . This can be made quantitative by measuring the phase persistence factor. This is given by the relative height of the secondary maximum of the correlation functions at $t = 16 \times 10^{-13}$ sec. In Table I this factor is

Table I

Molecular polarizability α and phase persistency ϕ for far infrared spectra of HCl in non-polar liquids

Solvent	Ar	Kr	Xe	SF ₄	CCl ₄	C ₆ H ₁₄
$\alpha(\text{\AA}^3)$	1.64	2.48	4.05	6.44	11	11
ϕ	0.005	0.009	0.013	0.020	0.000	0.000

given together with the polarizability of the solvent molecules. The fact that there is no correlation between these quantities shows that a picture of a HCl molecule performing a disturbed rotation in a static average potential field is totally inadequate. The actual movements of the solvent molecules as a function of temperature and density should be taken into account.

Therefore one can hope that a thorough study of a system such as HCl-argon with a detailed analysis of all the different experimental data will ultimately give real information about the molecular dynamics in the field.

The very concept of particle dynamics implies the assumption that the energy and momentum transfer are given by a product of two factors: the transfer effect per binary collision and the frequency of such collisions. The only other rigorous way of approach is to take collective motion coordinates as a starting point. For the class of systems we are discussing here the former method seems more appropriate because of the well defined rotational coordinate of HCl. We undertook to study the two factors, the effect of each collision and the frequency of the collisions. To determine the first factor we studied the temperature dependence of the linewidths of HCl in dilute argon gas. By the relation $\Delta\nu_{\frac{1}{2}} = \bar{\rho}\bar{v}\sigma$ a temperature dependent

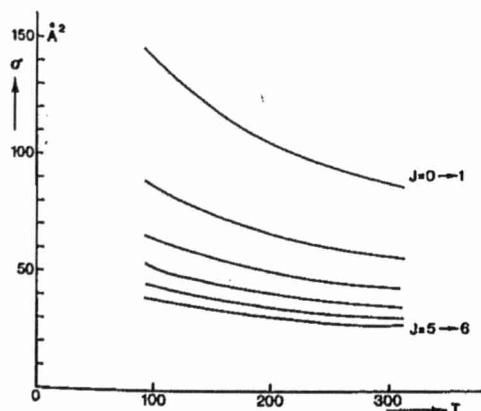


Fig.1. Linewidth crosssection vs temperature for some rotational lines of HCl perturbed by argon

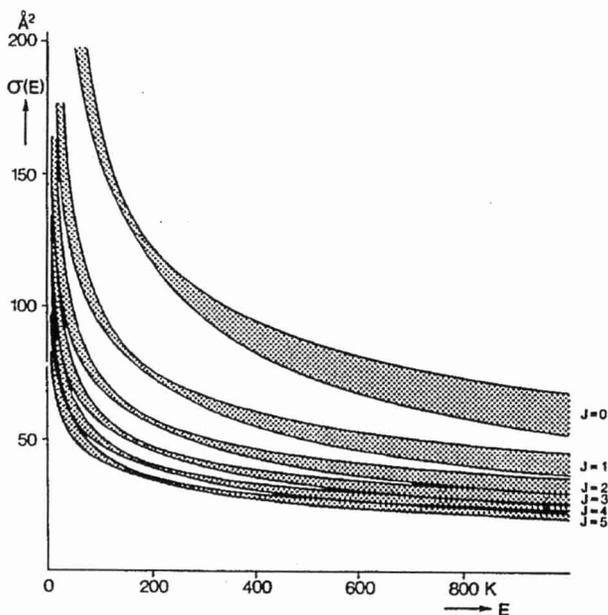


Fig.2. Linewidth cross-sections as a function of the relative kinetic energy of a colliding HCl-A pair

crosssection for each of the HCl rotational lines can be found by measuring the line halfwidth at two different but low densities of argon. An example of the results is shown in Fig.1. To facilitate the comparison with theory we transformed the temperature dependence into an energy dependence with the aid of the Maxwell distribution law and a simple Laplace transformation. The result is shown in Fig.2. The interpretation of the results can readily be made in terms of the semiclassical model which has been worked out completely by Neilson and Gordon [9,10].

The high crosssections for low energies stem mainly from elastic interactions of which a large part has a large impact parameter, especially for the lowest lines.

At higher energies the elastic contributions diminish rapidly. The inelastic part increases steadily and reaches a practically constant value once the sudden perturbation limit is attained. The contributions are here from the hard core collisions with low impact parameter. It is remarkable that the crosssection for the higher lines at high energies does not increase with energy as the model calculations predict. This means that even at higher energies a certain elastic contribution remains. It may also be that the repulsive part of the interaction potential is softer than has hitherto been assumed. The crosssections for HCl in krypton and xenon show a similar behaviour, and are for krypton slightly higher than for argon and

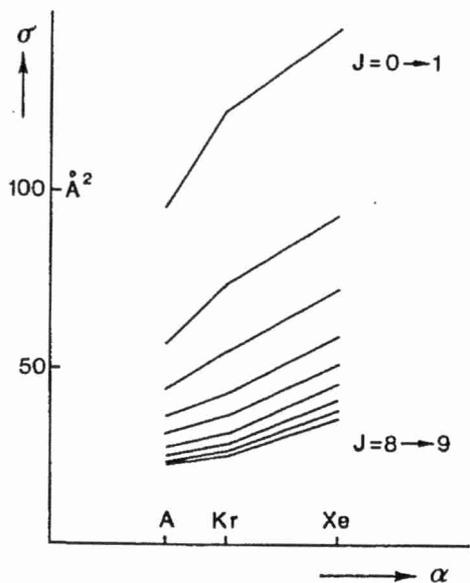


Fig.3. Linewidth crosssections of HCl rotational lines in three inert gases plotted vs the polarizability

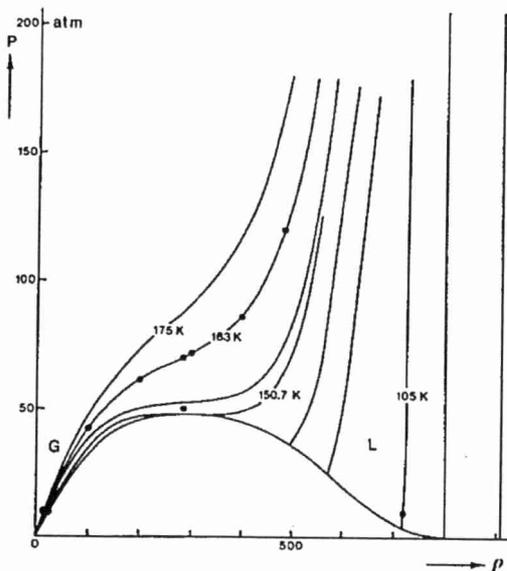


Fig.4. Phase diagram of argon. The dots indicate the points at which far infrared measurements of the HCl-argon system were made

for xenon slightly higher still.

Thus we have established the first factor, the collision effect. One should realize that already in the dilute gas when considering energy and momentum transfer with rotational degrees of freedom, a "collision" is not a very well defined event. An encounter between an HCl molecule and an argon atom with an impact parameter of about 5\AA and a relative kinetic energy of 150K , has a large effect on the first rotational line, with much momentum transfer and very little energy transfer. The same encounter has, however, an almost negligible effect on the 10th rotational line. In the former case the encounter is a collision, in the latter case the encounter is not a collision at all. The ensuing relation between transfer effect and collision frequency plays an important role at higher densities.

To establish the effect of the number of encounters we undertook the measurement of the HCl argon system at different densities. In Fig.4, the ρ - p phasediagram of argon, we indicated the points at which the measurements were made. An overall result of the spectra is given in Fig.5.

We shall here not go into details about efforts to explain the shape of these spectra in terms of different stochastic models [11,12]. To do this properly one has to calculate simulated spectra starting from

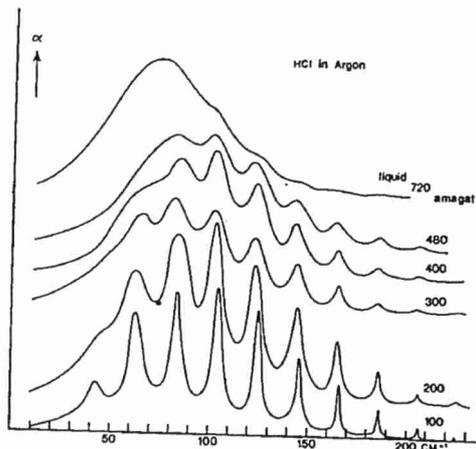


Fig.5. The far infrared spectra of HCl in argon at 163K and different densities

different model parameters.

There are, however, two ways open for a more empirical approach. One possible way is the comparison of the phase persistency of these spectra in dependence of the density, with the predicted collision time dependence of the phase persistency in a simple j -diffusion model [12]. Fig.6 shows this dependence for the j - and for the m -diffusion model. The inserted experimental points show that a j -diffusion model seems appropriate. If we now plot ϕ/ρ from the experiment versus $\phi/\frac{1}{T}$ from the model calculation we find a line that gives the deviation of the effective collision frequency from the collision frequency that follows from an extrapolation of a gas-model. Fig.7. The number of effective collisions lags behind with increasing densities to such an extent that a maximum is reached at about 500 am. The effective collision frequency in the liquid is even a little lower than at the supercritical density of 400 am.

The same effect can be found when we plot the estimated line halfwidth of the highest lines in the spectra which are still well defined, versus the density. Fig.8 shows the result for the $j = 7 \rightarrow 8$ and the $j = 9 \rightarrow 10$ line. It becomes now also clear that the effect in the phase persistency stems mainly from the high rotational lines. The broadening of the high rotational lines in the high density gas as well as in the liquid is far less than could be expected on the ground of a dilute gasphase extrapolation. This effect diminishes rapidly for the lines with lower initial j quantumnumbers.

Although we can now understand the composition of the overall spectra

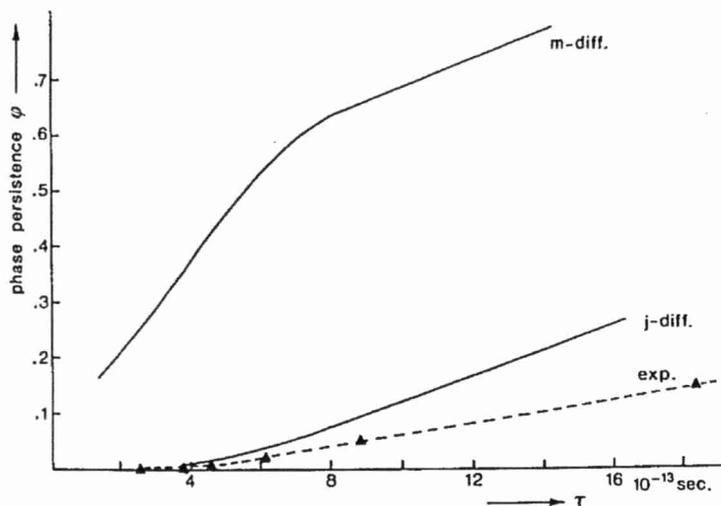


Fig.6. The theoretical prediction of the relation between phase-persistency and time between collisions

for the liquid and the high density gas: overdamped low lines, normally broadened lines in the medium frequency range and abnormally little damped lines in the high frequency, we still have not found the mechanism which is responsible for this behaviour.

The Enskog theory of dense gases [13] assumes that a high density system behaves just like a low density system, except that the number of collisions increases even faster than would follow from the increased

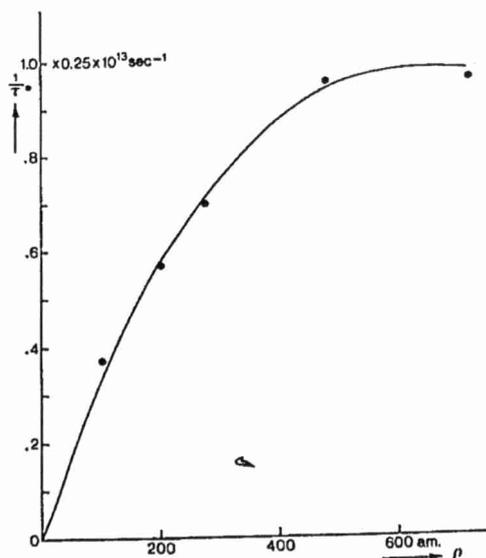


Fig.7. Plot of experimentally determined phase persistency divided by the density, versus the phase persistency divided by $1/\tau$ in the model calculation

density alone. This increase in collision number is brought about by the finite size of the atoms, which, although negligible with respect to the free path between collisions at low density, becomes at high densities comparable with the free path lengths. Quantitatively this effect is given by the value of the radial distribution function at the distance of two atoms at close contact, which equals the ratio between collision numbers at different densities.

This increase in number of collisions per second because of the finite size effect, becomes at still higher densities counterbalanced by a decrease in number because the atoms come so close together that they shield one another from atoms which are approaching from greater distance.

Although one might expect a fallacy here, the genuineness of this effect, which is commonly called backscattering, has clearly been demonstrated by molecular dynamics calculations [14,15]. The result is that although momentum is readily transferred, the movement of the particles over longer distances becomes strongly inhibited and the number of collisions dwindles accordingly.

The validity of the Enskog theory has of course intensively been tested with the normal transport properties of dense fluids where one considers

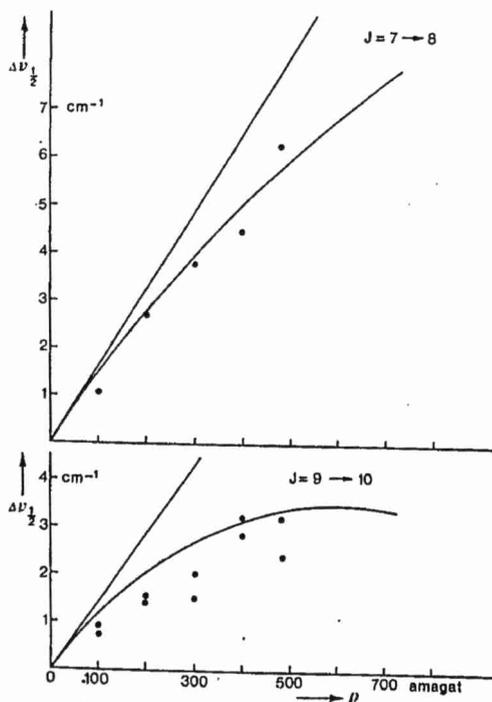


Fig.8. The linewidth of the 8th and 10th HCl rotational line in dependence of the argon density, the linear extrapolation from low density gasdata, the experimental points and the calculation based on backscattering

the transport of energy and momentum through a plane. Intuitive reasoning brings one to the surmise that the backscattering effect plays an even more important role for transport through a spherical surface around one particular molecule. The smaller the radius of that sphere is with respect to the radius of the shielding particles, the greater the shielding effect.

When we want to apply this observation to the high density HCl-argon system, we have to realize that the radius of the central sphere is given by the linewidth crosssections of the rotational line under consideration, whereas the relevant radius of the shielding particles is the normal hard core radius. With a simple calculation of the ratio between covered and uncovered surface of the central sphere, one can now estimate the reduced amount of collisions for the different rotational lines. The result is shown in Fig.8 for the 8th and 10th rotational line of HCl. The rough agreement which is obtained with the experimental results gives confidence in the indicated application of the Enskog theory. The experimentally observed spectral features can thus be interpreted in terms of this theory.

The excessive backscattering effect for linewidth crosssections so small that they become comparable with the hard sphere crosssections of argon, makes that the linewidths increase much slower than linearly with the density, possibly even slightly decrease with densities increasing from 500 to 700 am. This explains the occurrence of the high rotational lines of HCl in liquids such as argon, krypton, xenon and SF₆. The uniqueness of these examples stems from the fact that the frequencies of these transitions lie well above the frequency distributions of the medium, hence the

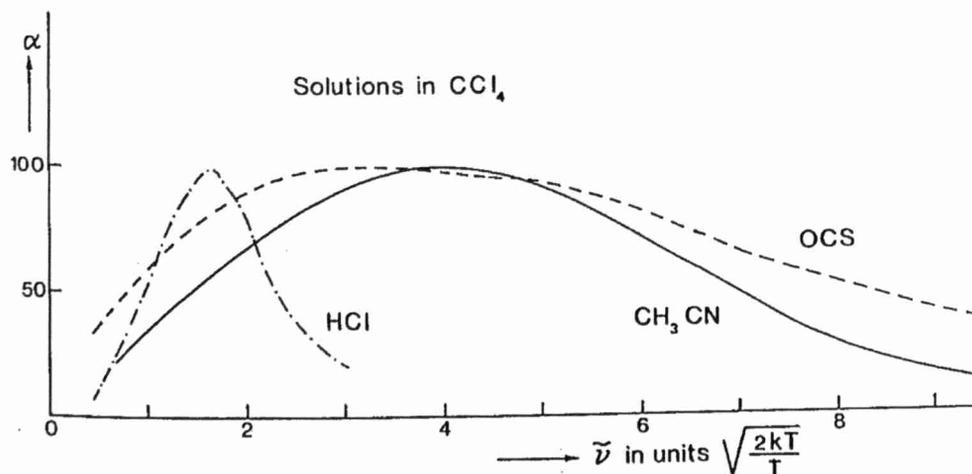


Fig.9. The far infrared spectra of different solutes in CCl₄ in reduced frequency units

small crosssections. The lower rotational lines have larger crosssections and hence there is far less effect of backscattering. The linewidths therefore increase much faster than linearly with the density and become overdamped. The general features of the far infrared spectra of these systems can therefore completely be understood. To obtain a quantitative agreement with calculated spectra starting with the line dependent collision numbers and the experimentally determined crosssections is very easy.

In this approach specific properties of the liquid phase come in gradually by the strong density dependence of the effect of backscattering. Not only does the shielding effect reduce the number of collisions but it also excludes some of the frequency components preferentially. The frequency distribution therefore loses some of its randomness. Backscattering has also as an effect that an argon atom which has collided with an HCl molecule may, after one intermediate collision, collide with the HCl molecule a second time. At very high densities these successive collisions may occur with a rather specific time interval. The effect will be that instead of a pure Poisson distribution of collisions there will be an enhanced probability of collision after a certain time. It has been shown before [11,12] that such peaked collision distribution functions when inserted into the usual rotational diffusion models give rise to spectra with an important absorption intensity in the higher frequencies. In particular it has been noticed that the maximum of the rotational absorption calculated with m - and j -diffusion models shifts to high frequencies completely in agreement with many experimental results. One could visualize this effect as a dipole-carrying elongated molecule, which, by successive back and forth collisions, comes to a librational movement. It is clear that an enhanced frequency component in the collision distribution can only have such an effect on the movement of the molecule if the molecule does

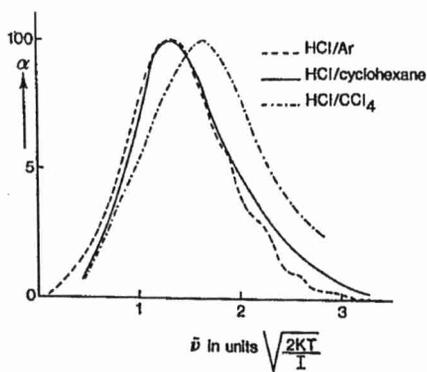


Fig.10. The far infrared spectra of HCl in different solvents in reduced frequency units

not rotate too fast, because this would have a randomising effect by itself. Most pronounced will the effect therefore be for molecules with a large moment of inertia. This is clearly demonstrated when we compare the spectra of HCl in CCl_4 at one hand and of OCS or CH_3CN in CCl_4 at the other

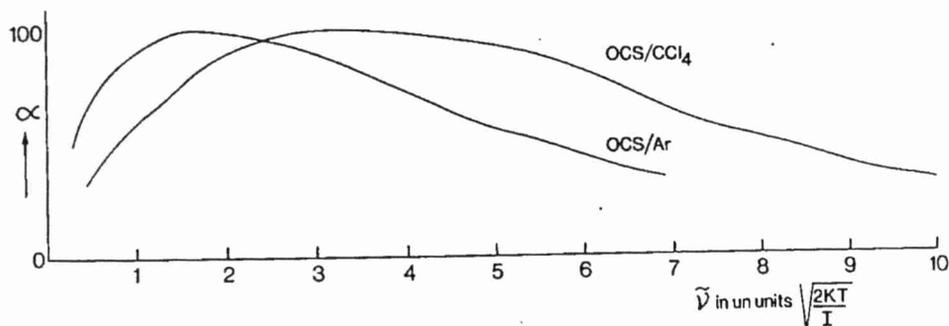


Fig.11. The far infrared spectra of OCS in different solvents in reduced frequency units

hand. Fig.9. In Fig.10 the spectra of HCl in argon, CCl_4 and $n\text{-C}_7\text{H}_{14}$ are compared. The larger crosssections of the high rotation lines in CCl_4 and $n\text{-C}_7\text{H}_{14}$, caused by the stronger interaction as compared with the noble gas media, make that no fine structure is observable. The low moment of inertia of HCl makes that an effect of the deviation from a Poisson distribution is barely visible. In Fig.11 a comparison of the spectra of OCS in argon and in CCl_4 shows that the deviation of the Poisson distribution in the latter case must be very large indeed, in accordance with the large moment of inertia and the large mass of CCl_4 . The spectrum of OCS in argon must be considered as a superposition of lines with large crosssections without much of a deviation of the Poisson distribution.

In conclusion it may be said that the far infrared absorption spectra of many different systems can be interpreted in terms of a collision model extended to high densities. If one properly introduces the phenomena that occur in the collision processes between finite size particles at high densities, there is no need for ad hoc introduction of assumed properties of dense fluids. The consistent use of the same language for the description of gases as well as for dense fluids can have a great advantage for the better understanding of the dynamical behaviour of the molecules.

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