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THE STATISTICAL CORRELATION BETWEEN ROTATION AND TRANSLATION: IMPLICATIONS FOR FINE AND HYPERFINE STRUCTURE IN QUANTUM MECHANICS

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ABSTRACT

For matrix isolated small molecules such as hydrogen deuteride (HD) the rotational spectra generated form the Schrodinger equation are perturbed by mixing with quantised translational lines which appear from the periodicity imposed by a solvent cage on the motion of the encaged HD molecule. The effect of the mixing of rotational and translational wave functions is that quantum translation/rotation effects occur in the final spectrum. There are shifts in rotational levels, broadening of rotational levels, and relaxation of rotational selection rules. In this paper it is shown that the existence of various new types of cross-correlation function in the laboratory and moving frames of reference implies the existence of new types of fine and hyperfine structure in the infra red spectrum of HD encaged in solvent molecules such as liquid argon. These new features could lead to specific and observable information on the nature of rotation to translation coupling in the liquid state of matter.

INTRODUCTION

This paper attempts to evaluate the effects on quantised spectral features of the statistical dependence of rotation upon translation in imperfect gases and liquids. The approach taken here to investigating the consequence for quantum mechanics of the existence of rotation/translation coupling in dilute gases is through the formal equivalence of the classical correlation function and the quantum mechanical inner product. [1,2] By making use of some results from a classical computer simulation of dilute gases it can be shown that some quantum mechanical inner products involving centre of mass linear velocity and molecular angular velocity and centre of mass position

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must exist both in the moving frame of reference defined by the three principal molecular moments of inertia and also direct in the laboratory frame (x,y,z). This must mean that some rototranslational quantum mechanical wave functions exist in the dilute gas and in the liquid in both frames of reference. Under certain conditions therefore the translational wave function and the rotational wave function mutually perturb each other and split the energy levels in a manner which may be observable spectroscopically. Usually, the eigenvalues of the linear momentum from Schrodinger's equation form a continuous spectrum stretching from minus infinity to infinity, [3] but in condensed matter, such as hydrogen deuteride, the translational energy levels become observable at intervals of about 100 cm^{-1} due to the periodicity imposed by the solvent molecules. This has been discussed by Ewing [4], and the experimental observations of the translational energy levels in hydrogen deuteride were reproduced quite accurately by a translational particle in the box model due to Friedmann et al. [5]. In the gas phase there is no periodicity of the translational motion, but it is clear from the latest molecular dynamics computer simulations [6-10] that the periodic rotational motion is correlated statistically to the centre of mass translational motion of the molecule in the moving frame (1,2,3). This means that the corresponding wave functions and quantum mechanical inner products also must exist in this frame and must have an influence on observable spectra [4] in the laboratory frame (x,y,z). The classical computer simulation results also prove that correlation functions exist in both frames of reference (1,2,3) and (x,y,z) that involves the centre of mass linear velocity $\underset{\sim}{v}$ and the angular velocity $\underset{\sim}{\omega}$ separately and simultaneously. An example of one of these autocorrelation functions is that of [11,12] the Coriolis force $2m\underset{\sim}{v} \times \underset{\sim}{\omega}$ where m is the molecular mass. Therefore in quantum mechanics the wave function and inner product corresponding to this force must also exist in both frames of reference. The rotational energy levels in a dilute gas and in a "quantum" liquid such as hydrogen deuteride [4] must therefore be perturbed and split by the existence of these rotation to translation wave functions. This might be the case in the gas phase, providing accurate experimental information on the nature of rotation to translation wave functions whose existence may be inferred by results as in this paper from the classical limit.

We use results from a classical computer simulation of the molecular dynamics of a dilute gas to infer the existence of wave functions in the moving and laboratory frames of reference by analogy with classical cross-correlation functions which appear in the simulation. This exercise is repeated for three types of molecule and is the classical equivalent to using a quantum mechanical hamiltonian in the Schrodinger equation and solving that equation for wavefunctions and inner products involving the simultaneous rotational and translational motion of the molecule. The results show qualitatively that it is possible to obtain detailed information about the mutual influence of rotation upon translation by studying the splitting of rotational levels by the translational motion of molecules in an imperfect gas, where the two kinds of motion are mixed by the mutual interaction of the force fields, i.e. through the potential energy term of the hamiltonian in Schrödinger's equation. Usually this kind of perturbation is thought to result merely in line broadening, but under favourable experimental conditions actual translational energy levels may be observed. [4] This may be the case for example in compressed hydrogen deuteride gas, where the translational motion is given some periodicity and where the infinite spectrum of eigenvalues for pure momentum is given periodicity and is simultaneously affected by statistical correlation with rotation. This paper suggests how such correlation may occur.

SURVEY OF CLASSICAL RESULTS

There have been several attempts to isolate the classical equivalent of the non vanishing inner product for rotation/translation wave functions. In the classical limit this is the cross-correlation function. It is not at all obvious how the non-vanishing c.c.f.'s can be discerned from the infinite number of possibilities, and most of the early attempts at doing this were confined to the attempted extension of the Debye theory of rotational diffusion in molecular liquids. The first attempt by Condiff and Dahler [13] was inspired by the hydrodynamical approach of the Kirkwood school. This was not successful because the complexity of the mathematics used obscured the physical implications. With the benefit of computers the situation has gradually become clearer over the last twenty years through the work of the Chicago and Brussels Schools and others. [14-22] The first cross-correlation of this type was finally isolated numerically in 1981 by Ryckaert et al. [21] using the moving frame (1,2,3) of the principal molecular moment of inertia. This was the first time that the time dependence of a simple rotation to translation c.c.f. had been isolated. This paper dealt with linear molecules and produced the first evidence for the existence of the classical cross-correlation function:

$$\langle \underset{\sim}{\omega}(t)\underset{\sim}{v}^{T}(o)\rangle_{(1,2,3)}$$

where the superscript T denotes transposition. Group theory was used to show that this simple type of cross-correlation must vanish by parity reversal symmetry in frame (x,y,z) in the absence of an electric field. Evans was the first to show [22] in 1985 that the application of an electric field $\underset{\sim}{E}$ promotes the existence of two elements of this cross correlation function directly in the lab. frame (x,y,z). For a z axis electric field these are the (x,y) and (y,x) elements. This result, also obtained by classical computer simulation, implies that the application of an electric field to compressed hydrogen deuteride gas or HD liquid would result in a splitting of the rotation/translation energy levels, a kind of rotation/translation Stark effect. In general for very light dipolar molecules such as HD or HT (tritium hydride) the electric field induced splitting of rotation/translation quantum lines should be observable with apparatus akin to that used in Stark splitting. If these lines are close together the double resonance techniques now available [23] should be used to interesting effect. Similarly a magnetic field should promote the existence of new translation/rotation lines in the lab. frame, through the existence of new inner products and wavefunctions. So far it has not been possible to simulate these even with classical methods, because the magnetic field introduces Lorentz forces difficult to deal with in conventional simulation. Once this technical difficulty is overcome the nature of magnetic field induced rotation/translation coupling should become observable direct in the laboratory frame. The experiment of perturbing the quantised rotation/translation spectral absorption lines of compressed HD or HT gas or liquids can proceed with conventional apparatus and should reveal shifts or splitting phenomena in the far infra red and microwave. Such phenomena would be the first direct experimental proof of the effect [22] of an external electric or magnetic (or indeed an electromagnetic laser) field on rotation/translation quantun lines. [4] The interpretation of these effects would need the information given in this paper on which of the inner products and wave functions of rotation/translation exist and which vanish, either in frame (1,2,3) or (x,y,z). The phenomena observable in HD or HT might also appear in other light molecules in the gas state or supercritical liquid state such as HF and ammonia. The motion of ammonia molecules is known to be quantised [24] in solvents such as SF_6 but translational energy levels such as those [4] in HD do not seem to have been isolated.

By looking at the spectrum of HD or HT or TD in a chiral solvent (the gas having been forced into the chiral liquid solvent under pressure, or mixed with a chiral gas under pressure) it ought to be possible to detect experimentally some signs of the different rotation/translation cross-correlation discovered for right and left hand enantiomers by Evans [9] in 1983. This discovery was again made by classical computer simulation.

By building on the work of Ryckaert et al. [21] and extending it to a range of different symmetries. Evans et al. have shown [6-9] that there exist several different types of fundamental cross-correlation in frame

(1,2,3). This is true even for the spherical top, T_d symmetry, where the simple cross-correlation function:

$$\langle \underset{\sim}{\omega}(t)\underset{\sim}{v}^T(o)\rangle_{(1,2,3)}$$

vanishes but higher order cross-and auto-correlations survive. The most recent work has shown that even in frame (x,y,z) the foundations of the great Debye theory [25] are undermined by the use of computer simulation. This is because of the existence in frame (x,y,z) of auto-correlations of the Coriolis, centripetal, and non-uniform molecular forces. [11,26] These appear directly from fundamental classical dynamics and involve simultaneously both the angular and linear variables of motion. For example, the Coriolis molecular force is

$$2m\underset{\sim}{v} \times \underset{\sim}{\omega}$$

where m is the mass of the rigid molecule, $\underset{\sim}{v}$ its centre of mass linear velocity and $\underset{\sim}{\omega}$ its angular velocity. Any textbook on fundamental dynamics will show [12] that the Coriolis force exists in frame (x,y,z). The centripetal force is an every day experience, and the non-uniform force is non zero in the presence of intermolecular force fields. All three types of molecular force appear directly in frame (x,y,z) even for the spherical top, [27] and in recent computer simulations their auto-correlation functions are clearly and unequivocally defined. [6-9, 26] All these forces were of course left out of consideration by Debye in the theory of rotational diffusion [25]. It is reasonable therefore to arrive at the conclusion that the theory has major shortcomings. Cross-correlations involving the three fundamental forces also exist [6-9,26] in frame (1,2,3) which implies that the forces themselves exist in frame (1,2,3) and also their auto-correlation functions in this frame. The auto-correlation functions are the same in frame (1,2,3) and (x,y,z) for the T_d symmetry spherical top but are different in time dependence for lower molecular symmetries.

The existence of these forces, their a.c.f.'s and their c.c.f.'s, may have been implicit in some of the elegant analytical work in this area, such as that of Steiger and Fox, [15] using many particle diffusion equations, or in the work on Brownian dynamics reviewed recently by Dickinson, [16] but there seems to be no explicit reference to these fundamental auto and cross-correlation functions in the analytical literature at present [13-20] excepting the work of the present author and co workers in attempting to respond [7] to the numerical results. The existence of these a.c.f.'s and c.c.f.'s in the classical limit implies the existence of the equivalent quantum mechanical wave functions and inner products, [1,2] in the liquid phase and in the gas phase if the translational energy spectrum is in any way discrete. Recent considerations have shown [27] that the use of group theory in frame (1,2,3) allows the comparison of the numerical results with symmetry predictions on the existence or otherwise of cross-correlation functions. This is useful to check the computer simulation algorithms. However, in the presence of a parity breaking field, [1,2,21,22] such as an electric field, the application of group theory becomes more difficult, and the surest results have so far been obtained by the methods of computer simulation. The methods of dielectric, and indeed all, spectroscopy depend [2] on the application to a sample of external fields, and this finding also has deep implications in the area of linear response theory and the Onsager reciprocal relations, where laboratory frame cross-correlation between fundamental variables are rarely considered in any analytical depth. Again, computer simulation was the first technique to show [9] that the dynamical properties of enantiomer pairs in frame (1,2,3) are not the same because one of the off diagonal elements of the cross-correlation tensor $\langle \underset{\sim}{v}(t)\underset{\sim}{\omega}^T(o)\rangle_{(1,2,3)}$ and that element only, switches sign for all t in frame (1,2,3). The same element vanishes for all t in the racemic mixture of right and left handed enantiomers. Group theory could perhaps have predicted this result, but did not, and to our knowledge there has not yet been an application of group theory to this problem of molecular dynamic in chiral media. The quantum mechanical equivalent of a cross-correlation matrix would be a matrix consisting of inner products as elements.

These examples are therefore sufficient to show that the pursuit of cross-correlations in molecular dynamics with computer simulation is an essentia spur to progress in this area, and in this spirit this paper explores new types of cross-correlation between molecular rotation, orientation, and translation in the gaseous phase of achiral asymmetric tops. The introduction of quantum mechanics into the computer simulation of molecular ensembles will allow this work to be extended to include bond vibration and cross-correlations between vibration, rotation and centre of mass translation. It would be interesting in the first instance to attempt to simulate with the computer the spectrum of hydrogen deuteride in the compressed vapour and liquid states of matter. [4]

COMPUTER SIMULATION METHODS

For each of three molecules chosen for this investigation a sample of 108 was chosen for the simulation on purely economic grounds. A time step of 5.0×10^{-15} sec was used for all three samples and this was small enough to produce satisfactorily constant total energy. Details of thermodynamic and inter molecular potential are given below for each sample.

CHLORINE DIOXIDE AND OXYGEN DICHLORIDE

These are triatomic C_{2v} asymmetric tops in which the mass distribution is much more isotropic than in the average asymmetric top. The pair potential for each molecule can be generated from the same atom atom Lennard-Jones parameters, those of oxygen and chlorine, [28] as follows:

$\sigma(o\text{-}o) = 2.8$ Å ; $\varepsilon/k(o\text{-}o) = 58.4$ K;

$\sigma(Cl\text{-}Cl) = 3.35$ Å; $\varepsilon/k(Cl\text{-}Cl) = 175.0$ K.

Chlorine dioxide was simulated at the density [28] of 0.309 gm per litre at 284 K in the gas phase. The bond length was 1.49 Å with a known [29] included angle of 118.5^{o} . Oxygen dichloride was simulated at 273 K with a density [29] of 0.0389 gm per litre. The literature bond length [28] is 1.70 Å and the included angle is 110.8^{o}. The mass of the chlorine atom is about twice that of the oxygen atom and in consequence the moment of inertia distribution is much like that of a symmetric top.

With these atom atom Lennard Jones parameters the total energy in the computer simulation was satisfactorily constant at a slightly positive value for chlorine dioxide and a more positive value for oxygen dichloride, indicating that both samples were in the gas phase, the positive kinetic energy being numerically greater than the negative potential energy so that the repulsive forces predominate over the adhesive in the simulation. The uncertainty in the pressure was also far less than that normally encountered in the simulation of a liquid at constant volume, a further indication that the sample is in the gas phase.

HYDROGEN SELENIDE

This is a C_{2v} triatomic asymmetric top with one very heavy central (S_e) atom attached to a very light hydrogen atom either side. It was simulated in the gas state at 300 K at a molar volume of 404.1 cm^3. A literature bond length of 1.47 Å was used with the known included angle of 91^{o}. The pair potential was mimicked with a three by three Lennard Jones potential with atom atom parameters as follows

$\sigma(H\text{-}H) = 2.40$ Å; $\varepsilon/k(H\text{-}H) = 21.1$ K;

$\sigma(Se\text{-}Se) = 3.90$ Å; $\varepsilon/k(Se\text{-}Se) = 218.0$ K.

It is known that hydrogen bonding in liquid hydrogen selenide, unlike liquid water, is negligible, and in consequence it was not considered necessary to mimick H bonding with for example an ST2 type of potential. The mass distribution in H_2Se is such that the Se atom is about 79 times heavier that each H atom. This makes the principal moment of inertia distribution very anisotropic, and in this paper we attempt to explore the consequences to the various cross-correlation functions of interest. A few results were also obtained for liquid hydrogen selenide just below the boiling point of 231.5 K at a literature molar volume of 40.41 cm^3 this allows one to contrast and estimate the cross correlation functions in the compressed gaseous and liquid states. The Lennard Jones parameters used in this simulation produced a pressure in the liquid satisfactorily constant at around one bar with the usual uncertainty of about five hundred bar; and in the gas the computed pressure achieved a value of about six bar, with a much smaller uncertainty of about 0.5 bar either side of the computed mean.

For each molecule the simulation of the cross correlation functions was carried out in frame (1,2,3) using at least two segments of about 2000 time steps each (1000 records of two time steps each). The auto correlation functions of the Coriolis, centripetal, and non uniform forces were built up in the same way in both frames (1,2,3) and (x,y,z). A representation of the noise level in the simulation can be achieved by illustrating the results from consecutive or different segments and hatching the difference between the curves so obtained. All correlation functions were constructed using running time averages with algorithms written by the author. Finally the integration of the classical equations of motion for the 108 molecules was achieved with the algorithm TETRA, full details of this algorithm have been given elsewhere, [29] and here we summarise its main features.

With reference to the rotational equations of motion for the 108 molecules the first step is the calculation of the torque from the resultant forces on each atom. The torque is evaluated at four points in time before being integrated numerically for the angular momentum. This integration proceeds in four stages, is relatively time consuming, but accurate. The translational equation of motion in TETRA is valid for the poly-atomic asymmetric top provided that this is rigid. It uses periodic boundary conditions and centre of mass to centre of mass cut off criteria. It uses periodic boundary conditions and centre of mass to centre of mass cut off criteria.

The number of atoms in each molecule and the number of molecules can be increased indefinitely provided the computer time is available. It incorporates corrections for long range forces and has facilities for using pair potentials of the site site type. For input temperature and molar volume the mean pressure is computed, together with the relevant thermodynamic parameters such as the mean internal energy, potential energy and translational and rotational kinetic energy. The run can be stopped and restarted at will, and therefore an indefinite number of steps can be used. The restrictions on time steps and number of molecules reported in this paper are purely economic in origin.

ANALOGY BETWEEN QUANTUM AND CLASSICAL MECHANICS [1,2]

Consider a linearly independent set $[A_j(t)]$, $j = 1,\ldots\ldots,n$ of real valued (implicitly) time-dependent dynamical variables of the given r-particle system. The set of all possible dynamical variables is a real Hilbert space. Now we construct an ensemble average in this space, denoted by the brackets $< >$. This is an inner product, so that

$$(A,B) = <A(o)B(t)>$$

where A and B are separate variables. The equilibrium canonical distribution function is

$$f(\underset{\sim}{\Gamma}_o) = \exp(-H(\underset{\sim}{\Gamma}_o)/kT) \;/\; \int e^{-H/kT}\, d\underset{\sim}{\Gamma}_o$$

where $\underset{\sim}{\Gamma}_o$ is $\underset{\sim}{\Gamma}$ at $t = 0$, and H is the hamiltonian. With this definition the inner product is:

$$(A^*,B) = \int d\underset{\sim}{\Gamma} f(\underset{\sim}{\Gamma})\; B(\underset{\sim}{\Gamma})\; A^*(\underset{\sim}{\Gamma})$$

The properties A and B depend on time only through the dependence of the state on time - they are implicitly time dependent. Therefore :

$$\dot{A} = i\hat{\mathcal{L}}\, A$$

has the formal solution:

$$A(\Gamma,t) = \exp\,(i\hat{\mathcal{L}}t)\; A\;(\Gamma,o)$$

and the time a.c.f. of A may now be defined as

$$c(t) = (A(t),\, A^*) = (e^{i\hat{\mathcal{L}}t}A,A^*)\ .$$

The scalar product used in quantum mechanics and the classical time correlation function are formally equivalent. More generally, two variables B and A can be used to construct a time cross-correlation function as follows :

$$c(t) = \int d\underset{\sim}{\Gamma} f(\underset{\sim}{\Gamma})A^*(\underset{\sim}{\Gamma})e^{i\hat{\mathcal{L}}t}A(\underset{\sim}{\Gamma}).$$

In analogy with quantum mechanics the two properties A and B are orthogonal if $(A^*,B) = 0$

The propagator $e^{i\hat{\mathcal{L}}t}$ is an orthogonal operator; and by analogy $f^{\frac{1}{2}}A \equiv \psi_A(\underset{\sim}{\Gamma})$ is a quantum mechanical wave function. This means that $c(t)$ is the expectation value of $e^{i\mathcal{L}t}$ in the state ψ_A.

With these definitions we shall show that the computer simulation produces cross correlation functions of the following type in frame (1,2,3) and (x,y,z).

IN FRAME (1,2,3)

The cross correlation functions $<\underset{\sim}{A}(o)\underset{\sim}{B}^T(o)>$ exist for $t > 0$. The vectors $\underset{\sim}{A}$ and $\underset{\sim}{B}$ are defined as in Table 1.

TABLE 1

Vector A	Vector B	Cross Correlation Function
$\underset{\sim}{v}$	$\underset{\sim}{\omega}$	$<\underset{\sim}{v}(t)\underset{\sim}{\omega}^T(o)>$
$\underset{\sim}{v} \times \underset{\sim}{\omega}$	$\underset{\sim}{v}$	$<\underset{\sim}{v}(t) \times \underset{\sim}{\omega}(t)\underset{\sim}{v}^T(o)>$
$\underset{\sim}{r} \times \underset{\sim}{\omega}$	$\underset{\sim}{r}$	$<\underset{\sim}{r}(t) \times \underset{\sim}{\omega}(t)\underset{\sim}{r}^T(o)>$
$\underset{\sim}{\omega} \times (\underset{\sim}{\omega} \times \underset{\sim}{r})$	$(\underset{\sim}{\omega} \times \underset{\sim}{r})$	$<\underset{\sim}{\omega}(t)\times(\underset{\sim}{\omega}(t)\times\underset{\sim}{r}(t))(\underset{\sim}{\omega}(o)\times\underset{\sim}{r}(o))^T>$

IN FRAME (x,y,z)

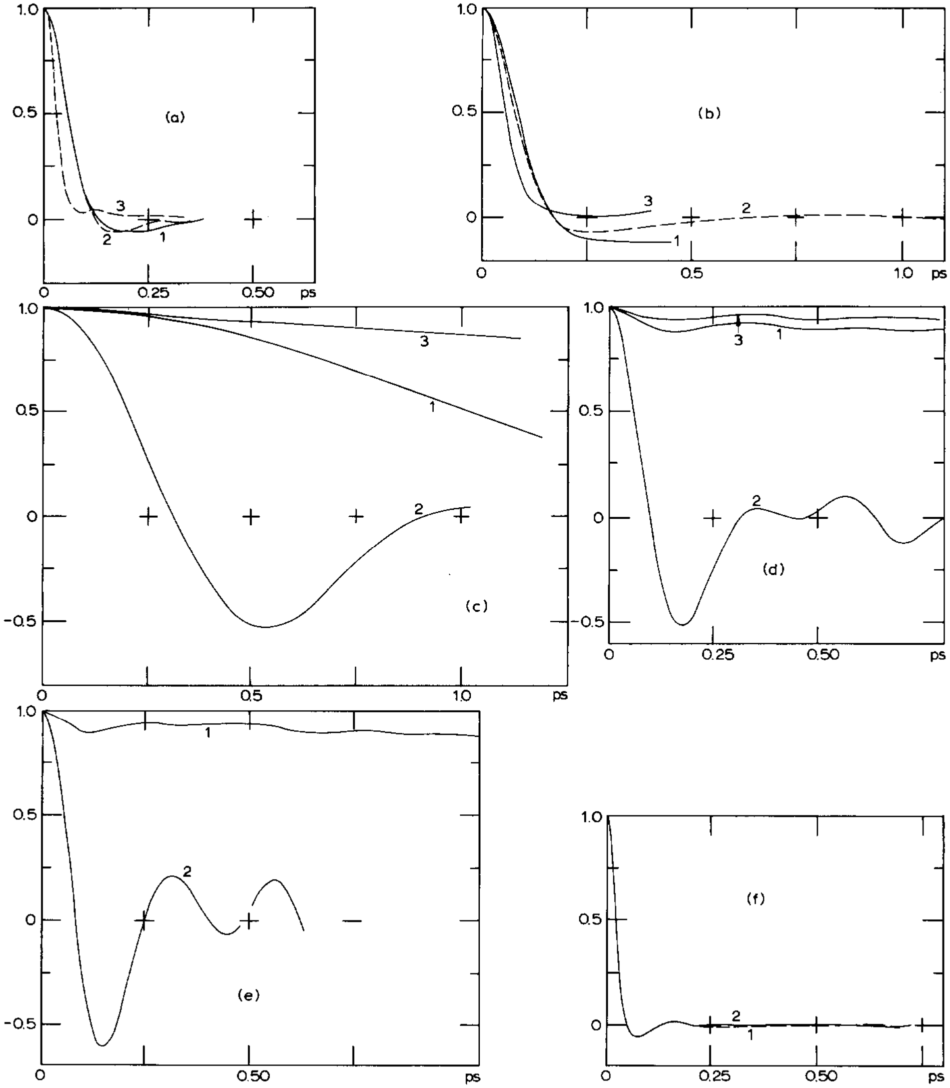
The autocorrelation functions of the Coriolis, centripetal, and non-uniform forces exist in frame (x,y,z) and the (x,y) and (y,x) elements of the laboratory frame cross correlation function $<\underset{\sim}{v}(t)\underset{\sim}{\omega}^T(o)>_{(x,y,z)}$ between linear and angular velocity exist [22] for a z axis electric field in frame (x,y,z). This means that the expectation values of the equivalent quantum states Ψ_{AB} must exist direct in the laboratory frame. It might therefore be reasonable to expect that the spectral absorptions corresponding to these states might become observable when a sample such as HD liquid or compressed HD gas is treated with an external electric field in the z axis of the laboratory frame. If this does indeed occur then it might be possible to identify with each line in the spectrum, or with each set of lines, a particular expectation value, which would be in classical terms a correlation function. This would lead to the first experimental method of directly identifying the very specific mechanisms of the correlations that exist between the vectors $\underset{\sim}{v}$,$\underset{\sim}{\omega}$ and $\underset{\sim}{r}$.

RESULTS AND DISCUSSION

In this section results are presented for auto and cross correlation functions in the gases chlorine dioxide, oxygen dichloride and hydrogen selenide in both frames of reference. These are expectation values in analogy with quantum mechanics, and their existence in the classical limit may be proof of spectral absorption lines which may be observable with HD as discussed already.

Perhaps the most significant effect from the point of view of the coupling in the laboratory frame is the existence of the autocorrelation functions of the Coriolis, centripetal and non-unifrom forces. These are illustrated in figure (1) for the samples in this paper. The existence of the Coriolis force in the laboratory frame is an inevitable consequence [26] of the fact that the (x,y,z) frame is a non-inertial frame with respect to the principal moment of inertia frame (1,2,3) in classical mechanics. Therefore we arrive at the obvious conclusion that in all polyatomics rotation can never take place without translation. This is exactly analogous to the well known theory [3] of Coriolis splitting caused by the fact that quantised vibration and rotation can never be independent of each other for the overwhelming majority of molecular symmetries. In quantum theory the effect of the Coriolis force generated by a simultaneously vibrating and rotating molecule is to split the vibrational energy level by an amount corresponding to the rotational energy levels. Similarly, in the quantum theory of a simultaneously rotating and translating polyatomic (or dipolar diatomic) the Coriolis force generated by the simultaneous rotation and centre of mass translation of the molecule would be to split the rotational energy levels by an amount corresponding to the translational energy levels, if these can be resolved. The practical problem is to choose those conditions (and samples) under which the translational energy levels are resolved and to choose the molecular symmetry under which Coriolis splitting occurs. In vibration rotation coupling the Coriolis splitting is observable only when the vibrational energy levels can be degenerate, [3] as in a symmetric top symmetric stretch, and Coriolis v/r splitting cannot occur in an asymmetric top where there are no degenerate energy levels. However quantum t/r (translation to rotation Coriolis splitting) does not seem to depend [4,5] on the existence of a degenerate vibrational mode of motion and there seems nothing to stop its occurrence in all dipolar symmetries, provided that the translational quantum lines are resolved and are infra red allowed, i.e. cause absorption in the infra red or far infra red and at lower frequencies.

To resolve translational quantum effects the mean free path must be longer than the dimensions of the hypothetical container which occurs in the standard particle in the box problem. [3] Therefore the study of HD in the dilute gas ought to be rewarded with the observation of rotational energy levels perturbed by splitting due to the translational effects whose classical mechanical counterparts are observed in this classical computer simulation.



A unique and elegant theoretical study of quantum mechanical t/r mixing has been carried out by Friedmann and Kimel, [5] using a perturbation method to account for the far infra red spectrum of HD in liquid argon. In HD, and in any molecule which is dipolar the coupling of rotational and translational motions are accounted for by Friedmann and Kimel [5] assuming a spherically symmetric cavity made up of the atoms of the argon solvent, rigid rotor wave functions, and isotropic harmonic oscillator translational wave functions. The effect of the coupling from perturbation theory was to give zero point translational energy to the rotational states and raise the J = 0,2,3 levels. The J = 1 level is however lowered by a near resonance with the 100 cm^{-1} translational quantum spacing. Other consequencies of the quantum mechanical t/r coupling are [4] that the rotational band widths of HD are doubled with respect to those of pure hydrogen or deuterium solutions in liquid argon. (There is of course t/r coupling of this type in H_2 and in D_2 but the rotation of these molecules is not infra red active). The rotational selection rules for HD are changed by mixing the translational and rotational wavefunctions. Besides the usual $\Delta J = 1$, there are $\Delta J = 2,3$ and 4 transitions observable, and this can be accounted for using perturbation theory which extensively couples translational and rotational wave functions. The perturbation theory

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Fig. 1 a) Autocorrelations of the Coriolis force for chlorine dioxide.

a) 1 First order autocorrelation function in the laboratory frame (x,y,z).
  2 First order, frame (1,2,3).
  3 Second order, both frames.

b) Autocorrelation functions of the non uniform force for oxygen dichloride,
  1 First order, frame (x,y,z).
  2 First order, frame (1,2,3).
  3 Second order, both frames.

c) Auto correlation functions of the Coriolis force, oxygen dichloride.
  1 First order, frame (x,y,z).
  2 First order, frame (1,2,3).
  3 Second order, both frames.

d) Autocorrelation functions of the Coriolis force, hydrogen selenide.
Notation as for fig. (1c).

e) Autocorrelation functions of the centrifugal force, hydrogen selenide.
Notation as for 1 First order laboratory frame.
  2 First order moving frame.

f) As for e) non uniform force.

by Friedmann and Kimel [5] does not specifically account for the Coriolis, non-uniform and centripetal forces observed in this paper, and it would be interesting to develop a quantum perturbation theory to do this and to account for the known experimental effects of quantum t/r coupling, i.e. shifts in rotational levels, broadening of rotational levels, and relaxation of selection rules. To these effects should be added splitting caused by the Coriolis force, and other effects caused by the existence in the laboratory frame of the centripetal and non-uniform forces whose "expectation values" i.e. the classical auto-correlation functions, are illustrated in figure (1). By extending the HD/argon work to the compressed gas a rich source of information should become observable on hyperfine effects of quantum t/r interaction. High resolution techniques, such as double resonance, could be used to observe the fine details of the splittings expected from the existence of the Coriolis force, as well as the various effects on the pure rotational selection rules. The same kind of effect should also become observable in the region of the vibrational absorption of the HD/argon system, where each vibrational line would be split into rotational sub levels, which would in turn be split into translational sub levels. By choosing conditions carefully, many more lines should become observable for the simple HD molecule than allowed in the pure rotational theory. By repeating the exercise for the more off-set rotor TH, tritium hydride, a different spectrum should be obtained providing more information on the details of t/r coupling. By repeating the whole experiment in the presence of a parity breaking field, [22] such as an electric field, many new splittings would probably appear. This would be in addition to the r/t splitting which Friedmann and Kimel [5] describe in detail and compare with the splitting observable in the fine structure in atomic energy levels, due to spin orbit interaction.

Fig. (1), although obviously obtained in the classical limit ("continuum approximation") shows that the simple treatment by Friedmann and Kimel [5] is incomplete, although powerful and elegant within its own terms of reference. The hamiltonian used by Friedmann and Kimel [5] is (in their notation):

$$H = H_o + v$$

with

$$H_o = \frac{p^2}{2m} + \frac{J^2}{2I} + 2\pi^2 c^2 \nu^2 m(r_G^2 + a^2)$$

Here $\underset{\sim}{r}$ designates the position vector of the so called centre of interaction, which is the sum:

$$\underset{\sim}{r} = \underset{\sim}{r}_G + a\underset{\sim}{l}_z$$

where a is the distance between the centre of interaction and the centre of mass and $\underset{\sim}{l}_z$ is a unit vector along the HD bond. The harmonic oscillator cell model

$$v'(r) = \tfrac{1}{2}kr^2 = 2\pi^2c^2\nu^2mr^2$$

is used to define the potential energy. Here ν is the frequency of the oscillation motion of the molecule in the cell in terms of $\underset{\sim}{r}_G$ and $\underset{\sim}{\Omega}$:

$$\frac{v'(r)}{2\pi^2c^2\nu^2m} = r^2 = r_G^2 + 2a\,\underset{\sim}{r}_G \cdot \underset{\sim}{l}_z + a^2$$

In this simple representation the coupling between rotation and translation is produced by the term:

$$\begin{aligned} v/(2\pi^2c^2\nu^2m) &= 2a\underset{\sim}{r}_G \cdot \underset{\sim}{l}_z \\ &= 2a(X\Phi_{x_z} + Y\Phi_{y_a} + Z\Phi_{z_z}) \end{aligned}$$

where Φ denotes direction cosines of the molecular axis z relative to the space fixed coordinate axes.

Although this treatment produces many interesting results (already summarised) concerning the rototranslational spectrum of liquid HD in an argon liquid lattice, clathrates and compressed gases it seems to leave out of explicit consideration the kinetic energy terms in the hamiltonian that arise from the existence in the laboratory frame (cf fig (1)) of the Coriolis force, $2m\underset{\sim}{\omega}x\underset{\sim}{v}$; the centripetal force $m\underset{\sim}{\omega}$ x $(\underset{\sim}{\omega}x\underset{\sim}{r})$; and the non-uniform force $m\dot{\underset{\sim}{\omega}}$ x $\underset{\sim}{r}$ of the HD molecule in the solvent cage. The energy terms corresponding to these forces would contain the force vectors to second order. In fig. 1 it is shown that the auto correlation functions of the second order vectors, e.g. that of the Coriolis vector dotted into itself:

$$\frac{<([2m\underset{\sim}{\omega}(t)\ x\ \underset{\sim}{v}(t)].[2m\underset{\sim}{\omega}(t)\ x\ \underset{\sim}{v}(t)]).([2m\underset{\sim}{\omega}(o)\ x\ \underset{\sim}{v}(o)].[2m\underset{\sim}{\omega}(o)\ x\ \underset{\sim}{v}(o)])>}{16m^4<(\underset{\sim}{\omega}(o)\ x\ \underset{\sim}{v}(o).\underset{\sim}{\omega}(o)\ x\ \underset{\sim}{v}(o))^2>}$$

exist in the laboratory frame (x,y.z), and being scalars, invariant to frame transformation, are identical in time dependence in the moving frame (1,2,3).

The hamiltonian considered by Friedman and Kimel [5] should contain terms in the kinetic energy which come from the non-inertial terms, the Coriolis energy, the centripetal energy and the non uniform energy. A fuller quantum mechanical analysis would involve these terms and lead, following the analysis of Friedmann and Kimel, [5] to a spectrum rich in structure. In this analysis the effect of the external z axis electric field would be to promote the existence of the classical cross-correlation function:

$$<\underset{\sim}{\omega}(t)\underset{\sim}{v}^T(o)>_{(x,y,z)}$$

directly in the laboratory frame (x,y,z). The extra term in the hamiltonian due to the electric field would be [30] (to first order):

$$-\underset{\sim}{\mu} \cdot \underset{\sim}{E}$$

where $\underset{\sim}{\mu}$ is the molecular dipole moment of HD. This breaks the symmetry of the hamiltonian to time reversal and affects the whole of the quantum analysis given by Friedmann and Kimel. The effect of the electric field would be closely analogous to Stark splitting.

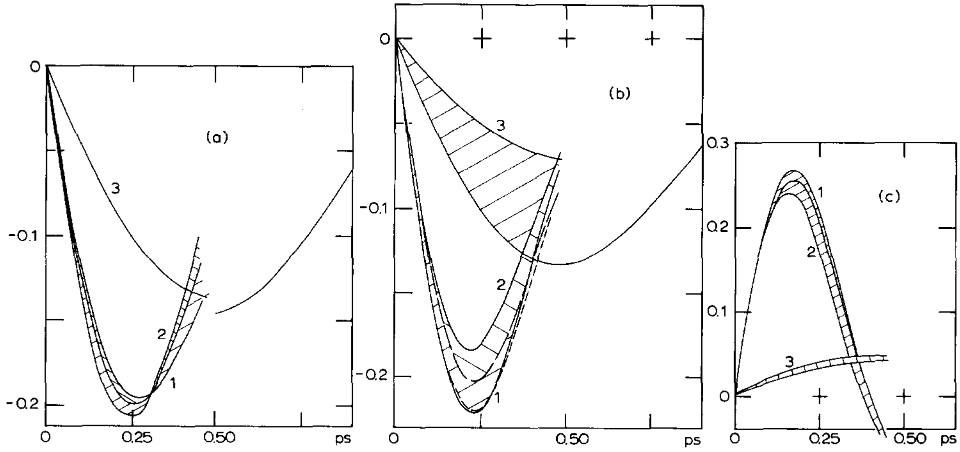

Fig. 2. a) The cross correlation function between the Coriolis acceleration and the linear velocity in frame (1,2,3) for chlorine dioxide gas.
1) (1,1) element; 2) (2,2) element; 3) (3,3) element.
b) The cross correlation $<\underset{\sim}{r}(t) \times \underset{\sim}{\omega}(t)\underset{\sim}{r}^T(o)>$, notation as for a).
c) The cross correlation $<\underset{\sim}{\omega}(t) \times (\underset{\sim}{\omega}(t) \times \underset{\sim}{r}(t))(\underset{\sim}{\omega}(o) \times \underset{\sim}{r}(o))^T>$, as for a).

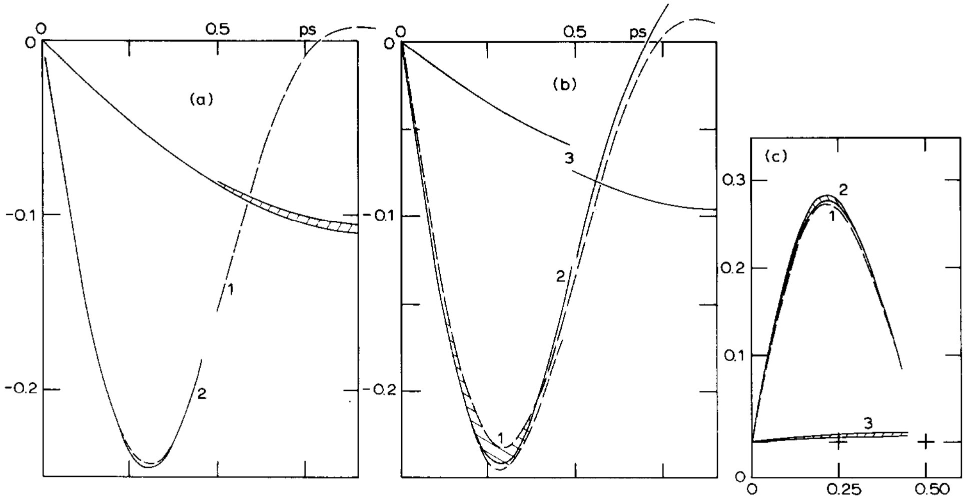

Fig. 3. As for figure (2), oxygen dichloride.

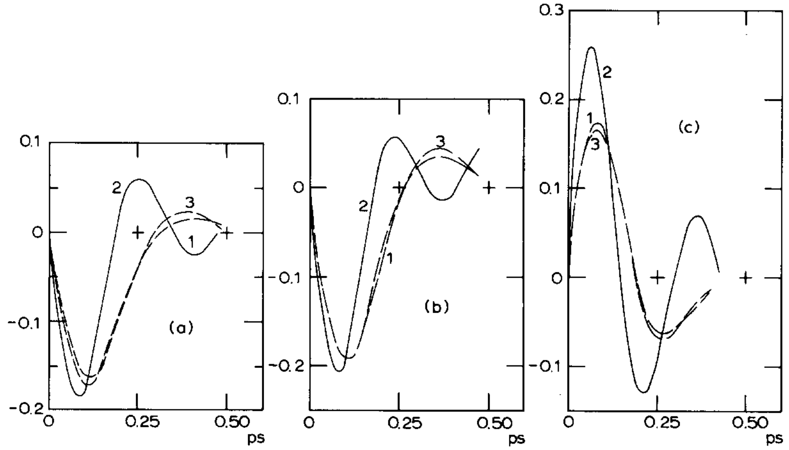

Fig. 4. As for fig. (2), hydrogen selenide.

In addition to the laboratory frame forces whose autocorrelation functions are illustrated in fig. (1) the cross correlations listed in Table 1 are observable for chlorine dioxide, oxygen dichloride and hydrogen selenide in the rotating frame of reference. These are illustrated in figs (2) to (5) and it is clear that the position vector, as in the treatment of Friedmann and Kimel, plays an important role in determination of the non vanishing cross-

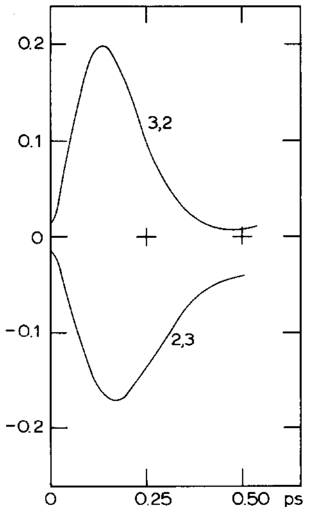

Fig. 5. Elements of the cross correlation function $\langle \underset{\sim}{v}(t)\underset{\sim}{\omega}^T(o)\rangle$ for liquid hydrogen selenide. In the dilute gas these elements become very small.

correlation functions in frame (1,2,3). The cross-correlation functions in figs. (2) to (5) all vanish however in the laboratory frame (x,y,z). A complete quantum mechanical treatment would have to be capable of reproducing this result correctly for all molecular symmetries.

CONCLUSION

A rich field of investigation could be available for exploration if the quantum mechanical consequencies of the classical results of the simulation in this paper were to be used to predict the details in a high resolution study of rotation-translation spectra in cage isolated small molecules such as HD. The existence of such forces as the Coriolis force between the molecular centre of mass velocity and its own angular velocity; the centripetal force and the non uniform force suggests that the quantum spectrum, computed with the method of Friedmann and Kimel [5], would be very rich in fine and hyperfine detail, due to the intricate but highly selective nature of the inevitable statistical correlation between molecular rotation and translation in frames (x,y,z) and (1,2,3). The experimental conditions would have to be chosen very carefully so as to maximise the chances of seeing translation energy levels and hyperfine structure due to t/r coupling. The predicted effect of an electric field, judging from the available classical computer simulation results, would be to promote the existence of direct t/r correlations in frame (x,y,z) and therefore more fine and hyperfine structure in analogy with the Stark effect. Double resonance techniques could be employed to measure the hyperfine structure in, for example, matrix isolated HD at low temperatures.

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