

THE STATISTICAL CORRELATION BETWEEN ROTATION AND TRANSLATION IN A DILUTE GAS

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ABSTRACT

The rotation and translation of a molecule in a dilute and moderately compressed gas are shown to be correlated statistically in the laboratory frame of reference (x,y,z) and the frame of the principal molecular moments of inertia (1,2,3). This means that in the classical limit it is no longer sufficient to base a kinetic theory of, for example, line broadening, on the factorisation of energy into rotational and translational components. Various types of cross-correlation are demonstrated in both frames of reference for oxygen dichloride in the dilute gas and for chlorine dioxide in the moderately compressed gas.

If we introduce the concept of quantum translation then it is possible that the existence of this type of cross correlation function in quantum mechanics might lead to the appearance of new absorption lines which are not accounted for in the theory of rotational absorption. The experimental detection of such lines could serve as the first evidence for the existence of quantum translation.

INTRODUCTION

There does not seem to exist at present a kinetic theory of gases which takes into account the fact that the molecules in a gas both rotate and translate. The present available theories, such as the M and J diffusion models of Gordon [1-4] are incomplete in the sense that only the net rotational motion is described, and the centre of mass linear velocity is left out of specific consideration. Recent computer simulations in the liquid phase have shown [5-10] that the statistical correlation between molecular rotation and translation can be observed in detail in the frame

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Dedicated to Professor W.J. Orville-Thomas

of reference defined (see eqn. (1)) by the three principal axes of the molecular moments of inertia, (1,2,3). In this paper the investigation is extended to the compressed and dilute gas phases of chlorine dioxide and oxygen dichloride, two simple, triatomic, asymmetric tops. The computer simulation algorithm is adapted for this purpose from a standard constant volume algorithm designed for liquid phase studies. The results for standard auto-correlation functions such as those of the molecular linear velocity, angular velocity, orientation and rotational velocity for the dilute gas indicate that the computer simulation method produces the expected theoretical results for the dilute gas, when these are known. For example the orientational and rotational velocity autocorrelation functions are Kummer functions, as expected theoretically [11], and the linear velocity and angular momentum autocorrelation functions decay very slowly. Therefore the use of periodic boundary conditions does not seem to be a problem, even for simulations of a dilute gas. Having established this the computer simulation method is used in this paper to investigate dilute gas properties which do not seem to be known in kinetic theory, such as the purely rotational M and J diffusion theory. These include a variety of cross-correlation functions between rotation and translation, and also auto-correlation functions in frame (1,2,3) and also in frame (x,y,z) which involve both rotational and translational variables simultaneously. Therefore the simulation provides a great deal of extra information which is not available in conventional kinetic theory of dilute gases [12]. This information involves the moving frame of reference and the molecular centre of mass linear velocity directly. The existence of such moving frame cross-correlations poses the following questions:

- i) Is it possible to develop a theory of collision broadening which is capable of describing experimentally observable features (e.g. in the far infra red) [13] self-consistently with the cross-correlations given here for the first time?
- ii) Do some of these cross-correlations and autocorrelations appear directly in frame (x,y,z) and if so under what conditions? How do they influence experimentally observable properties [14] in the gas phase?

#### COMPUTER SIMULATION ALGORITHM

For each of the two molecules a sample of 108 molecules was used with standard periodic boundary conditions [15], and a time step of  $5.0 \times 10^{-15}$  sec, small enough to produce a satisfactory constant total energy. For each sample this quantity remained constant to well below 0.01%.

## THE MOLECULES

Both chlorine dioxide and oxygen dichloride are triatomic asymmetric tops in which the mass distribution is fairly isotropic around two axes. They are both nearly symmetric tops. The pair potential for each molecule was generated with the same Lennard-Jones atom-atom terms [16].

$$\begin{aligned}\sigma(\text{O} - \text{O}) &= 2.8 \text{ \AA} ; & \epsilon/k(\text{O} - \text{O}) &= 58.4 \text{ K}; \\ \sigma(\text{Cl} - \text{Cl}) &= 3.35 \text{ \AA} ; & \epsilon/k(\text{Cl} - \text{Cl}) &= 175.0 \text{ K} .\end{aligned}$$

Chlorine dioxide was simulated in the mildly compressed gas at a molar volume corresponding to a density of 0.309 gm per litre at 284 K. The bond length was 1.49  $\text{\AA}$  with a known [17] included angle of  $118.5^\circ$ . Oxygen dichloride was simulated at 273 K with a density of 0.0389 gm per litre in the dilute gas at 273 K. The literature bond length is 1.70  $\text{\AA}$  and the included angle is  $110.8^\circ$ . The mass of the chlorine atom is about twice that of the oxygen atom and in consequence the moment of inertia distribution is such that each molecule is nearly 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.

For each molecule the simulation was used to construct a variety of auto- and cross-correlation functions in frames (x,y,z) and (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 [18] were built up in the same way in both frames (x,y,z) and (1,2,3).

## RESULTS AND DISCUSSION

## Oxygen Dichloride in the Dilute Gas

Fig. (1) illustrates clearly the effect of the rotating frame on the centre of mass linear velocity auto-correlation function, which in frame (x,y,z) is a very slowly decaying function of time. The effect of the moving

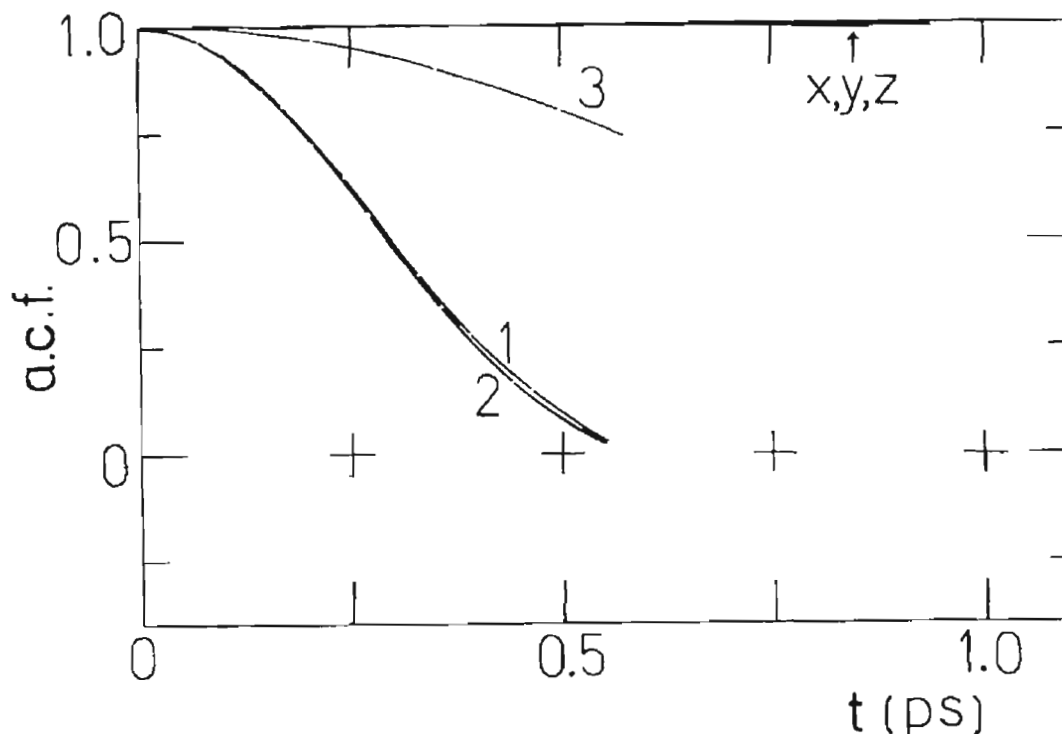


Figure 1. Linear velocity auto-correlation functions for dilute oxygen dichloride gas. (x,y,z) Laboratory frame auto-correlation function.

- 1)  $\langle v_1(t)v_1(0) \rangle / \langle v_1^2 \rangle$  ;
- 2)  $\langle v_2(t)v_2(0) \rangle / \langle v_2^2 \rangle$  ;
- 3)  $\langle v_3(t)v_3(0) \rangle / \langle v_3^2 \rangle$  .

frame (1,2,3) is to make the three component linear centre of mass velocity a.c.f.'s in this frame decay anisotropically and much more quickly than in frame (x,y,z). This is because frame (1,2,3) is rotating and translating simultaneously. This is one of the effects that a fuller and more complete kinetic theory of molecular gases should attempt to match. Note that two components of the moving frame component auto-correlation functions in fig. (1) are nearly equal in time dependence, the third, component 3, is very different. The basic reason for this is that oxygen dichloride is nearly a symmetric top.

Fig. (2) is the equivalent of fig. (1) for the molecular angular velocity a.c.f. In the laboratory frame (x,y,z) this decays more quickly than the centre of mass linear velocity a.c.f. of fig. (1), but again the components in the moving frame are anisotropic and have different time dependences. This is a clear indication that linear velocity is having an effect on the rotational velocity in the moving frame running-time averages. This is basically important for the development of the theory of Brownian motion to involve the linear velocity,  $\underline{v}$ , on an equal footing with the angular velocity  $\underline{\omega}$  in the moving frame (1,2,3) in which the Euler/Langevin equations are written. This

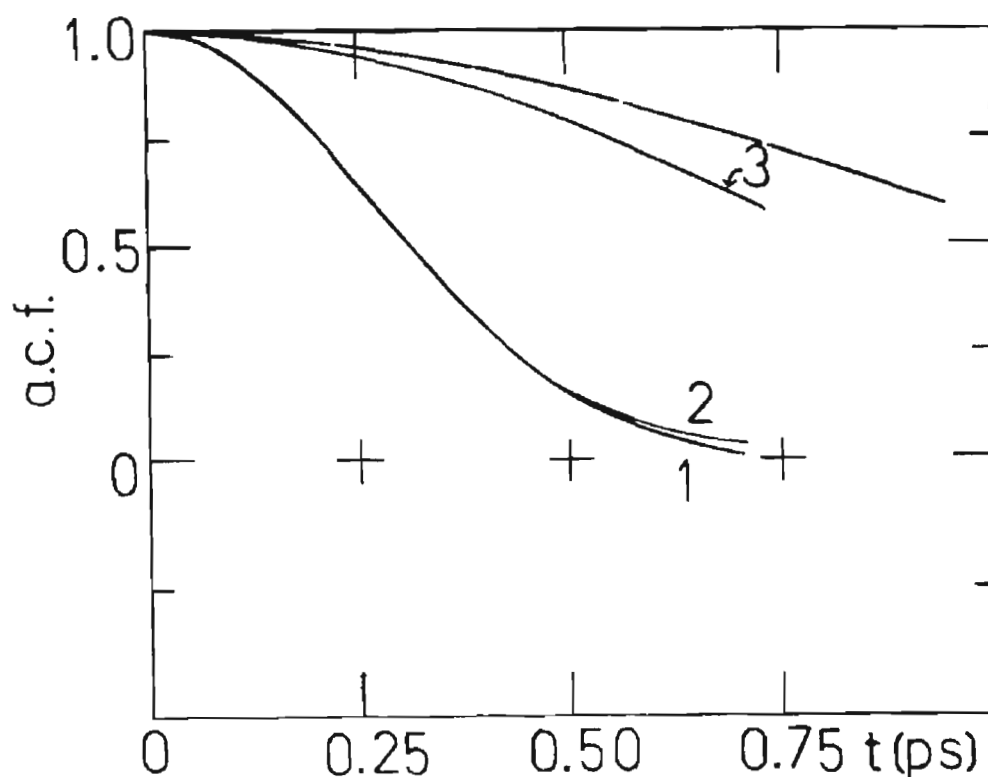


Figure 2. Angular velocity auto-correlation functions for dilute oxygen dichloride.

-----  $[\langle \underline{\omega}(t) \cdot \underline{\omega}(0) \rangle / \langle \omega^2 \rangle]_{(x,y,z)}$

- 1)  $\langle \omega_1(t) \omega_1(0) \rangle / \langle \omega_1^2 \rangle$  ;
- 2)  $\langle \omega_2(t) \omega_2(0) \rangle / \langle \omega_2^2 \rangle$  ;
- 3)  $\langle \omega_3(t) \omega_3(0) \rangle / \langle \omega_3^2 \rangle$  .

is also basically true for kinetic theory in anything except the mathematical limit of free rotation. This limit only applies in an infinitely dilute gas, where the total energy is kinetic energy, the intermolecular potential energy having vanished. Only in this limit is translation uncorrelated from rotation.

For the rotational velocity auto-correlation functions the computer simulation provides results reminiscent [11] of the Kummer function for the symmetric top. Similarly for the orientational auto-correlation functions. This is strong evidence for the fact that the algorithm is producing the correct theoretical curves (the Kummer functions) in the limit of dilute gas dynamics. Of course the Kummer functions only apply strictly speaking in the infinitely dilute gas, but the simulation of oxygen dichloride reported in this paper is carried out under conditions where collisions are still effective, but which are at the same time approaching the free rotor limit.

In recent work [5-10] computer simulations of molecular liquids have uncovered the existence of several different types of cross-correlation function which can be observed in frame (1,2,3). In addition, some auto-correlation functions involving both the rotational and linear velocity, such as the a.c.f. of the molecular Coriolis acceleration, can be observed in both frames (x,y,z) and (1,2,3). This means that the accepted analytical descriptions of molecular dynamics, both via kinetic theory and Brownian motion, are very restricted in scope. The present authors have made attempts to extend the theory of Brownian motion to rototranslation, and have produced a set of Langevin equations for this purpose [8]. However there is no method of solving these analytically except perhaps with the usual drastic assumptions of Brownian motion theory [19]. Fig. (3) illustrates one of the cross-correlation

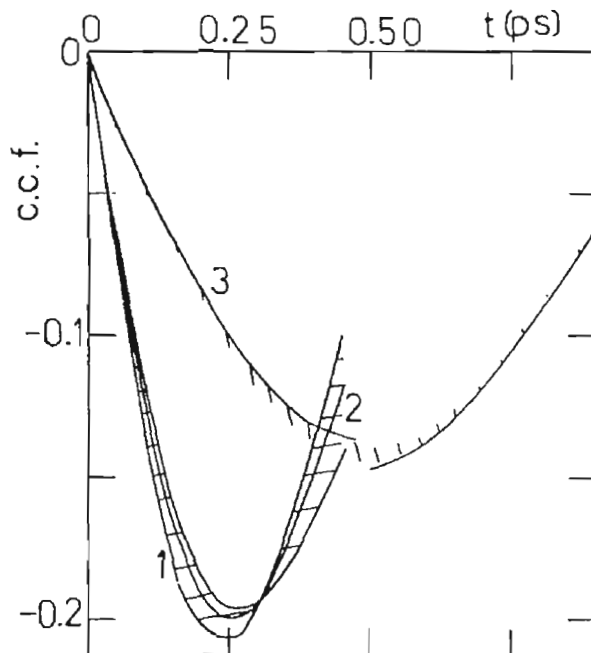


Figure 3. Cross-correlation functions for compressed chlorine dioxide gas in the moving frame of reference.

- 1)  $\langle (\underline{v}(t) \times \underline{\omega}(t))_1 v_1(0) \rangle / (\langle v^2 \rangle \langle \omega^2 \rangle^{\frac{1}{2}})$  ;
- 2)  $\langle (\underline{v}(t) \times \underline{\omega}(t))_2 v_2(0) \rangle / (\langle v^2 \rangle \langle \omega^2 \rangle^{\frac{1}{2}})$  ;
- 3)  $\langle (\underline{v}(t) \times \underline{\omega}(t))_3 v_3(0) \rangle / (\langle v^2 \rangle \langle \omega^2 \rangle^{\frac{1}{2}})$  .

functions from the present simulation in frame (1,2,3). This is the cross-correlation in frame (1,2,3) (see eqn. (1)) between the Coriolis linear acceleration in that frame and the same molecule's linear centre of mass velocity in that frame. It is important to the development of a more comprehensive kinetic theory of gases because it is a fundamental molecular

cross-correlation function which the theory cannot describe. In other words a comprehensive kinetic theory of gases would be capable of producing experimental data, but would also be capable of generating non-vanishing cross-correlation functions entirely self-consistently. Therefore the time dependence of fig. (3) is a fundamental challenge to the analytical theory. There seems to be no contemporary method of producing this result analytically from the kinetic theory of imperfect gases, i.e. the theory of collisional broadening. Nevertheless the amplitude of the c.c.f.'s in fig. (3) is very large, much greater than that observable in liquids, reaching some 25 per cent of the denominator. This means that the conventional theory of kinetics in imperfect gases has a major defect in that it cannot be used to describe a variety of results from the computer simulation. Similarly fig. (4) shows equivalent results to fig. (3) for the cross-correlation function  $\langle \underline{r}(t) \times \underline{\omega}(t) \underline{r}^T(0) \rangle$  in frame (1,2,3) and fig. (5) for the c.c.f.  $\langle \underline{\omega}(t) \times (\underline{\omega}(t) \times \underline{r}(t)) (\underline{\omega}(0) \times \underline{r}(0))^T \rangle$ .

Here  $\underline{r}$  is the position vector of the centre of mass of the molecule. It is defined in frame (x,y,z) in such a way that the mean  $\langle \underline{r}(t) \rangle$  over the 108 molecules in the "cube" vanishes, and also the correlation function be defined as:

$$\langle \underline{r}(0) \cdot \underline{r}(0) \rangle / \langle r^2(0) \rangle \equiv 1$$

$$\langle \underline{r}(t) \cdot \underline{r}(0) \rangle / \langle r^2(0) \rangle \rightarrow 0 \quad t \rightarrow \infty$$

The vector  $\underline{r}$  may be defined in frame (1,2,3) by eqn. (1), with  $\underline{A} \equiv \underline{r}$ .

The general synopsis for kinetic theory becomes even cloudier in figs. (6) and (7), where the auto-correlation functions of the Coriolis, centripetal and non-uniform molecular forces are shown for illustration in both frames of reference (see appendix 1). These results show that any theory which leaves out of consideration the linear velocity is not complete even in the laboratory frame (x,y,z). It is useful to note in figs. (6) and (7) that the second order a.c.f.'s.

$$C_{\text{cor2}} = \frac{\langle \underline{v}(t) \times \underline{\omega}(t) \cdot \underline{v}(t) \times \underline{\omega}(t) \times \underline{\omega}(t) \underline{v}(0) \cdot \underline{v}(0) \times \underline{\omega}(0) \rangle}{\langle (\underline{v}(0) \times \underline{\omega}(0) \cdot \underline{v}(0) \times \underline{\omega}(0))^2 \rangle}$$

$$C_{\text{num2}} = \frac{\langle \underline{r}(t) \times \dot{\underline{\omega}}(t) \cdot \underline{r}(t) \times \dot{\underline{\omega}}(t) \underline{r}(0) \times \dot{\underline{\omega}}(0) \cdot \underline{r}(0) \times \dot{\underline{\omega}}(0) \rangle}{\langle (\underline{r}(0) \times \dot{\underline{\omega}}(0) \cdot \underline{r}(0) \times \dot{\underline{\omega}}(0))^2 \rangle}$$

are identical in both frames to five places of decimals. This shows that

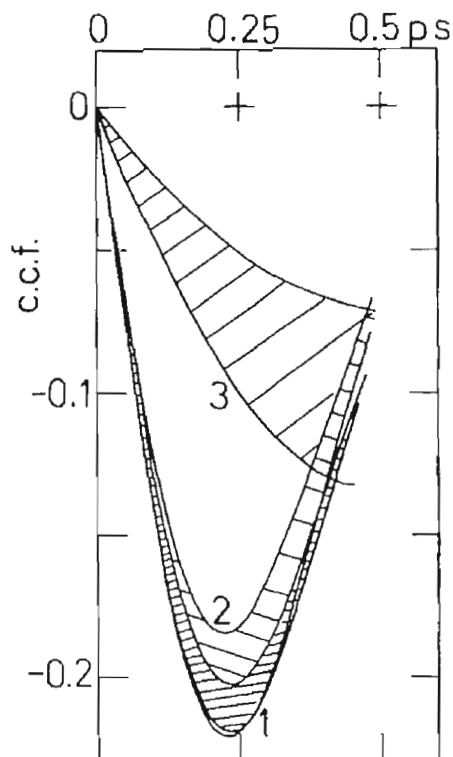
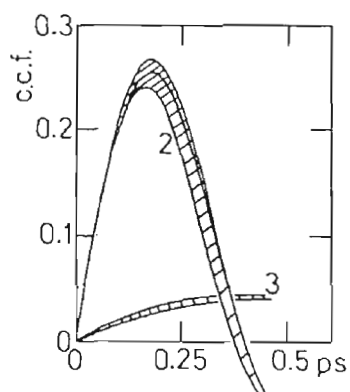


Figure 4 Cross-correlation functions for compressed chlorine dioxide gas in the moving frame of reference.

- 1)  $\langle (\underline{r}(t) \times \underline{\omega}(t))_1 r_1(0) \rangle / (\langle r^2 \rangle \langle \omega^2 \rangle^{\frac{1}{2}})$  ;
- 2)  $\langle (\underline{r}(t) \times \underline{\omega}(t))_2 r_2(0) \rangle / (\langle r^2 \rangle \langle \omega^2 \rangle^{\frac{1}{2}})$  ;
- 3)  $\langle (\underline{r}(t) \times \underline{\omega}(t))_3 r_3(0) \rangle / (\langle r^2 \rangle \langle \omega^2 \rangle^{\frac{1}{2}})$  .

Figure 5 Cross-correlation functions for compressed chlorine dioxide gas in the moving frame of reference.



- 1)  $\langle (\underline{\omega}(t) \times (\underline{\omega}(t) \times \underline{r}(t)))_1 (\underline{\omega}(0) \times \underline{r}(0))_1 \rangle$  ;
- 2)  $\langle (\underline{\omega}(t) \times (\underline{\omega}(t) \times \underline{r}(t)))_2 (\underline{\omega}(0) \times \underline{r}(0))_2 \rangle$  ;
- 3)  $\langle (\underline{\omega}(t) \times (\underline{\omega}(t) \times \underline{r}(t)))_3 (\underline{\omega}(0) \times \underline{r}(0))_3 \rangle$  .



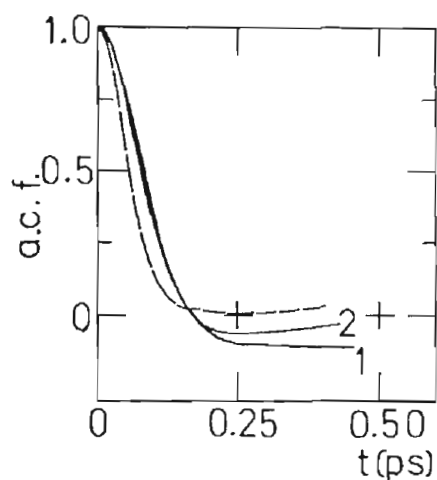


Figure 6 First and second order autocorrelation functions of the non-uniform  $\dot{\underline{w}}(t) \times \underline{r}(t)$  in the laboratory and moving frames of reference: oxygen dichloride

- 1) First order a.c.f. in the laboratory frame  $(x,y,z)$
- 2) First order a.c.f. in the moving frame of reference  $(1,2,3)$ .
- Second order a.c.f. in both frames.

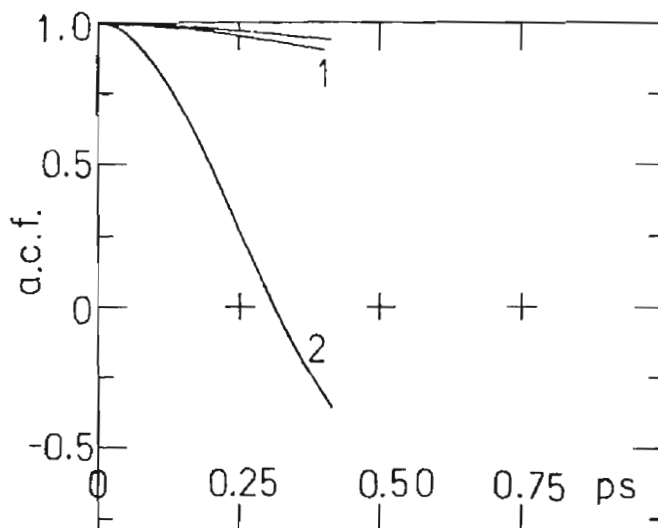


Figure 7 First and second order autocorrelation functions of the Coriolis force  $2m\underline{v}(t) \times \underline{\omega}(t)$  in the laboratory and moving frames of reference: oxygen dichloride

- 1) First order a.c.f. in the laboratory frame  $(x,y,z)$
- 2) First order a.c.f. in the moving frame of reference  $(1,2,3)$
- Second order a.c.f. in both frames.

the algorithms generating these data are correct, because the second order a.c.f. is a scalar in both frames, and therefore invariant to frame transformation. This is important evidence to show that the auto-correlation functions being computed in this paper are not numerical artifacts, because the expected result in respect of the second order functions is achieved to better than five decimal places in both frames of reference. The laboratory frame results in figs. (6) and (7) therefore show that the kinetic theory of imperfect gases is basically lacking in the consideration of laboratory frame autocorrelation functions which show up for the first time in this computer simulation. It is interesting to note, furthermore, that the a.c.f.'s of the non-uniform force on  $\underline{r}(t) \times \underline{\dot{\omega}}(t)$  have a similar time dependence in both frames, with what appears to be a long negative tail, but the a.c.f.'s of the Coriolis force,  $2m\underline{v} \times \underline{\omega}$ , have a very different time decay, that in the moving frame (fig. (7)) being much the faster, in line with the laboratory and moving frame behaviour of the a.c.f.'s taken individually of  $\underline{v}$  and  $\underline{\omega}$ .

#### CHLORINE DIOXIDE

A similar pattern of statistical correlation between dynamical variables also exists for chlorine dioxide in the moderately compressed gas and in this section we concentrate on a new type of cross-correlation. This is illustrated here for chlorine dioxide but also exists for oxygen dichloride. This correlates the orientational vectors and their time derivatives into the centre of mass linear velocity,  $\underline{v}$ . The investigation begins in this paper with the simplest type, a three by three tensor whose elements in the moving frame of reference may exist for  $t > 0$  depending on the molecular geometry and point group symmetry (see appendix 2). This type was first introduced by Ryckaert et al. [20] and by Evans et al. [21] for cross-correlations between the molecular angular velocity  $\underline{\omega}$  and  $\underline{v}$ . The computer simulation results of this work for the cross-correlation functions:

$$\begin{aligned} \langle \underline{e}_1(t) \underline{v}^T(0) \rangle_{(1,2,3)} & ; \quad \langle \underline{e}_2(t) \underline{v}^T(0) \rangle_{(1,2,3)} & ; \quad \langle \underline{e}_3(t) \underline{v}^T(0) \rangle_{(1,2,3)} & ; \\ \langle \dot{\underline{e}}_1(t) \underline{v}^T(0) \rangle_{(1,2,3)} & ; \quad \langle \dot{\underline{e}}_2(t) \underline{v}^T(0) \rangle_{(1,2,3)} & ; \quad \langle \dot{\underline{e}}_3(t) \underline{v}^T(0) \rangle_{(1,2,3)} & . \end{aligned}$$

where  $\underline{e}_1$ ,  $\underline{e}_2$  and  $\underline{e}_3$  are unit vectors in the axes 1,2 and 3 of the principal molecular moments of inertia, show that some of the elements of these cross-correlation tensors do in fact exist for  $t > 0$ . This allows us to conclude that the reorientational dynamics of these asymmetric tops are not statistically independent of the linear centre of mass velocity. This result may or may not

be implied by theories of hydrodynamics, such as those of mode/mode coupling used in the theory of light scattering in liquids, but it seems that this is the first evidence from direct computer simulation at a single molecule level of their existence.

#### CONSIDERATIONS OF FRAME TRANSFORMATION

Some care needs to be taken in defining the orientational unit vectors  $\underline{e}_1, \underline{e}_2, \underline{e}_3$  and their time derivatives in the moving frame of reference. In general the vector  $\underline{A}$  can be transformed from frame (1,2,3) to frame (x,y,z) and vice-versa using cartesian transformation. The components of the vector  $\underline{A}$  in frame (1,2,3) are generated from those in frame (x,y,z) for each molecule of the ensemble as follows:

$$A_1 = A_x e_{1x} + A_y e_{1y} + A_z e_{1z}$$

$$A_2 = A_x e_{2x} + A_y e_{2y} + A_z e_{2z} \quad 1$$

$$A_3 = A_x e_{3x} + A_y e_{3y} + A_z e_{3z}$$

This transformation can be carried out for each of the orientation vectors and time derivatives which are therefore defined in frame (1,2,3) by:

$$(e_1)_1 = e_{1x} e_{1x} + e_{1y} e_{1y} + e_{1z} e_{1z}$$

$$(e_1)_2 = e_{1x} e_{2x} + e_{1y} e_{2y} + e_{1z} e_{2z} = 0 \quad 2$$

$$(e_1)_3 = e_{1x} e_{3x} + e_{1y} e_{3y} + e_{1z} e_{3z} = 0 \quad ,$$

$$(e_2)_1 = e_{2x} e_{1x} + e_{2y} e_{1y} + e_{2z} e_{1z} = 0$$

$$(e_2)_2 = e_{2x} e_{2x} + e_{2y} e_{2y} + e_{2z} e_{2z} \quad 3$$

$$(e_2)_3 = e_{2x} e_{3x} + e_{2y} e_{3y} + e_{2z} e_{3z} = 0 \quad ,$$

$$(e_3)_1 = e_{3x} e_{1x} + e_{3y} e_{1y} + e_{3z} e_{1z} = 0$$

$$(e_3)_2 = e_{3x} e_{2x} + e_{3y} e_{2y} + e_{3z} e_{2z} = 0 \quad 4$$

$$(e_3)_3 = e_{3x} e_{3x} + e_{3y} e_{3y} + e_{3z} e_{3z} \quad ,$$

$$(\dot{e}_1)_1 = \dot{e}_{1x} e_{1x} + \dot{e}_{1y} e_{1y} + \dot{e}_{1z} e_{1z}$$

$$(\dot{e}_1)_2 = \dot{e}_{1x} e_{2x} + \dot{e}_{1y} e_{2y} + \dot{e}_{1z} e_{2z} \quad 5$$

$$(\dot{e}_1)_3 = \dot{e}_{1x} e_{3x} + \dot{e}_{1y} e_{3y} + \dot{e}_{1z} e_{3z} \quad ,$$

$$\begin{aligned}
 (\dot{e}_2)_1 &= \dot{e}_{2x}e_{1x} + \dot{e}_{2y}e_{1y} + \dot{e}_{2z}e_{1z} \\
 (\dot{e}_2)_2 &= \dot{e}_{2x}e_{2x} + \dot{e}_{2y}e_{2y} + \dot{e}_{2z}e_{2z} \\
 (\dot{e}_2)_3 &= \dot{e}_{2x}e_{3x} + \dot{e}_{2y}e_{3y} + \dot{e}_{2z}e_{3z}
 \end{aligned} \tag{6}$$

$$\begin{aligned}
 (\dot{e}_3)_1 &= \dot{e}_{3x}e_{1x} + \dot{e}_{3y}e_{1y} + \dot{e}_{3z}e_{1z} \\
 (\dot{e}_3)_2 &= \dot{e}_{3x}e_{2x} + \dot{e}_{3y}e_{2y} + \dot{e}_{3z}e_{2z} \\
 (\dot{e}_3)_3 &= \dot{e}_{3x}e_{3x} + \dot{e}_{3y}e_{3y} + \dot{e}_{3z}e_{3z}
 \end{aligned} \tag{7}$$

From basic physical considerations each of the vectors  $\underline{e}_1$ ,  $\underline{e}_2$ , and  $\underline{e}_3$  have no components in mutually orthogonal axes of frame (1,2,3), but this is not necessarily true for the time derivatives  $\dot{\underline{e}}_1$ ,  $\dot{\underline{e}}_2$  and  $\dot{\underline{e}}_3$ . These derivatives are important in the theory of far infra-red absorption by molecular liquids and can be generated from the orientation vectors through the basic kinematic relations:

$$\left\{ \dot{\underline{e}}_i = \underline{\omega} \times \underline{e}_i \right\} (x,y,z) \tag{8}$$

of the laboratory frame (x,y,z). These kinetic relations are true irrespective of whether the centre of mass of the molecule is moving or not. Therefore the cross-correlations between the derivative vectors  $\dot{\underline{e}}_1$ ,  $\dot{\underline{e}}_2$ , and  $\dot{\underline{e}}_3$  and the linear centre of mass velocity  $\underline{v}$  are in one sense triple correlations between the orientation vectors  $\underline{e}_1$ ,  $\underline{e}_2$  and  $\underline{e}_3$ , the molecular angular velocity  $\underline{\omega}$  and the linear velocity  $\underline{v}$ ; all vectors defined in the moving frame (1,2,3). This triple correlation involves orientation, angular velocity, and linear velocity and it is but a small step to extend the analysis conceptually to triple correlations between vibration, rotation, and translation in frame (1,2,3). In the first instance the vibration along the orientation vector could be treated classically, for example with Hooke's Law.

Figs. (8) and (9) show the non-vanishing cross correlation elements in the moving frame between the rotational velocity vectors and the linear centre of mass velocity. It seems that for each of the principal rotational velocities two elements of the cross-correlation function matrix exist above the noise in figs (8) and (9) for the slightly compressed chlorine dioxide gas. This has the consequence that the infra red spectrum of the compressed gas is never purely rotational in origin, and must always be a compound, statistically speaking, of rotation and translation. This criticises the usual approach to infra red spectroscopy where the energy of a gas phase molecule is treated as if it possessed several distinct reservoirs of energy

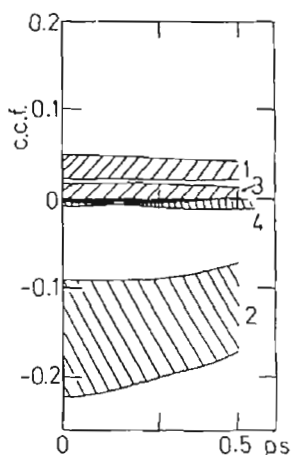


Figure 8 Compressed gaseous chlorine dioxide, cross correlations in the moving frame (1,2,3) between the rotational velocity vector  $\dot{e}_1$  and the linear centre of mass velocity vector  $v$  in the moving frame.

$$1) \quad \langle \dot{e}_{12}(t)v_3(o) \rangle / (\langle \dot{e}_{12}^2 \rangle^{1/2} \langle v_3^2 \rangle^{1/2})$$

$$2) \quad \langle \dot{e}_{13}(t)v_2(o) \rangle / (\langle \dot{e}_{13}^2 \rangle^{1/2} \langle v_2^2 \rangle^{1/2})$$

$$3) \quad \langle \dot{e}_{12}(t)v_1(o) \rangle / (\langle \dot{e}_{12}^2 \rangle^{1/2} \langle v_1^2 \rangle^{1/2})$$

$$4) \quad \langle \dot{e}_{11}(t)v_2(o) \rangle / (\langle \dot{e}_{11}^2 \rangle^{1/2} \langle v_2^2 \rangle^{1/2})$$

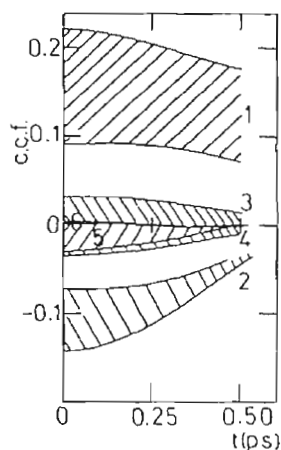


Figure 9 As for fig. (10) for the rotational velocity vector  $\dot{e}_2$ .

$$1) \quad \langle \dot{e}_{21}(t)v_2(o) \rangle / (\langle \dot{e}_{21}^2 \rangle^{1/2} \langle v_2^2 \rangle^{1/2})$$

$$2) \quad \langle \dot{e}_{22}(t)v_1(o) \rangle / (\langle \dot{e}_{22}^2 \rangle^{1/2} \langle v_1^2 \rangle^{1/2})$$

$$3) \quad \langle \dot{e}_{23}(t)v_1(o) \rangle / (\langle \dot{e}_{23}^2 \rangle^{1/2} \langle v_1^2 \rangle^{1/2})$$

$$4) \quad \langle \dot{e}_{22}(t)v_3(o) \rangle / (\langle \dot{e}_{22}^2 \rangle^{1/2} \langle v_3^2 \rangle^{1/2})$$

$$5) \quad \langle \dot{e}_{23}(t)v_2(o) \rangle / (\langle \dot{e}_{23}^2 \rangle^{1/2} \langle v_2^2 \rangle^{1/2})$$

$$6) \quad \langle \dot{e}_{21}(t)v_3(o) \rangle / (\langle \dot{e}_{21}^2 \rangle^{1/2} \langle v_3^2 \rangle^{1/2})$$

so that the total energy may be split up between different reservoirs.

It is well known that in this theory rotational spectra should consist of a simple set of lines at frequencies given by  $2BJ$  (for linear and symmetric top molecules). This is a great over simplification, and real spectra consist of many more lines. Rotation-vibration coupling within a molecule is equally well known to result in the splitting of quantum lines (Coriolis splitting and l type doubling), and the coupling of whole molecule rotation with nuclear orientation is well known and developed theoretically and experimentally. These effects are all present in the infinitely dilute gas. In the imperfect gas (in all practical situations) the results of the classical computations of this paper show that there is strong statistical correlation in the laboratory and moving frames of reference between the rotation of the whole molecule (assumed rigid) and the translation of its own centre of mass. This effect appears in the moving frame in a variety of ways and in the laboratory frame through the existence of the auto-correlation function of the Coriolis force generated by the combined rotational and translational motion of the molecule. This Coriolis force (which should be distinguished very carefully from the well known intra molecular Coriolis force in a vibrating and rotating molecule) can only be significant when the moving molecule encounters, and is influenced by, the force field of other molecules in a thermodynamic ensemble. If it is possible to treat translation as being quantised in the same way as rotation then it should be possible to evaluate the quantum mechanical equivalent of the classical Coriolis, non-uniform, and centripetal forces discovered in this work and to establish a new theory of quantum spectroscopy in imperfect gases. It should then be possible to discern whether the hypothetical quantum translation to rotation correlation results in the appearance of new spectra lines which could be discerned experimentally. In the classical simulation of this paper there are no quantum lines, of course, and in the classical limit the effect of considering translation in a rotational theory would be to broaden and sharpen continuum spectra in the far infra red, such as those actually observed experimentally in moderately compressed gases. The effect of hypothetical quantum translation on dilute gas spectra might be to break selection rules and to cause multiplicity in high resolution spectra such as those obtained by infra red radio frequency double resonance. The situation would be of particular interest in chiral gases, where the cross correlations would be different in frame (1,2,3) for the enantiomers and the mixture. Some experimental evidence is already available [14] for this effect in a recent infra red/radio frequency double resonance investigation of the enantiomer and racemic mixture of a chiral vapour. This then might well turn out to be the first evidence for the existence of quantum translation

in dilute gases or compressed vapours. This is because there seems to be [14] more lines in the far infra red/radio frequency spectrum of the enantiomer than the racemic mixture for some pump laser frequencies and less for others. There is no classical explanation for this effect, which, however, awaits corroboration.

With the use of quantum mechanics in computer simulation the above approach could be verified by direct numerical investigation, using quantum mechanics both for translation and rotation.

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#### APPENDIX 1

##### On the Existence in Frame $(x,y,z)$ of the Non Inertial Linear Velocity and Accelerations

Confusion sometimes occurs concerning the existence in frame  $(x,y,z)$  of the dynamically non inertial linear velocity and linear accelerations, typified by the centripetal or Coriolis acceleration. The nomenclature in this context is misleading due to historical development, the accelerations being known as the "pseudo accelerations". They are "pseudo" because they do not appear in the three laws of motion of Newton, which operate in dynamically inertial frame of reference. This does not mean that they do not exist. Many texts on dynamics go to great lengths to emphasise that the Coriolis acceleration is real, and so is the centripetal acceleration [18]. They occur whenever there is rotational motion superimposed upon Newtonian velocity or acceleration. The purpose of this appendix is to attempt to show as clearly as possible the origin of these acceleration, and to show that they exist in frame  $(x,y,z)$ . Eqn. (1) then implies immediately that they also exist in frame  $(1,2,3)$  simply by setting the general vector  $\underline{A}$  of that equation to centripetal acceleration or Coriolis acceleration as the case may be.

The nature of the non inertial velocity, accelerations and higher time derivatives thereof is revealed the most clearly by using [8] a frame of reference  $(1,2,3)'$  whose origin is the same as the origin of  $(x,y,z)$  but which rotates with respect to  $(x,y,z)$  with an angular velocity  $\underline{\omega}$ . It follows that  $(x,y,z)$  rotates with respect to  $(1,2,3)'$  at the same angular velocity, a seemingly trivial but important corollary. With this frame definition it is possible to bring into consideration a basic theorem of dynamics linking

the differential operator  $\underline{D}_f$  in the frame (x,y,z) to its ( $\underline{D}_m$ ) counterpart in frame (1,2,3)'. If the operations are on the molecular centre of mass position vector  $\underline{r}$  then the theorem is

$$\underline{D}_f \underline{r} \equiv (\underline{D}_m + \underline{\omega x}) \underline{r} \quad (\text{A1})$$

and its corollary is

$$\underline{D}_m \underline{r} \equiv (\underline{D}_f - \underline{\omega x}) \underline{r} \quad (\text{A2})$$

These equations can be written in the more familiar notation:

$$[\underline{v}]_{(x,y,z)} \equiv [\underline{v} + \underline{\omega x r}]_{(1,2,3)}, \quad (\text{A3})$$

$$[\underline{v}]_{(1,2,3)} \equiv [\underline{v} - \underline{\omega x r}]_{(x,y,z)} \quad (\text{A4})$$

Here  $[\underline{v}]_{(x,y,z)}$  is the linear centre of mass velocity defined with respect to frame (x,y,z). Eqn. (A3) shows that this is equivalent to a sum of two terms in frame (1,2,3)'. These are the Newtonian velocity  $[\underline{v}]_{(1,2,3)}$ , and the non inertial linear velocity  $[\underline{\omega x r}]_{(1,2,3)}$ , each defined with respect to frame (1,2,3)'. The importance of the corollary, eqn (A4), is that the reverse is true, implying the existence of the term  $[\underline{\omega x r}]_{(x,y,z)}$  in the laboratory frame (x,y,z). This is the non inertial linear velocity, which has the same dimensions as the Newtonian linear velocity  $[\underline{v}]_{(x,y,z)}$ . It follows, quid erat demonstrandum, that the non-inertial linear velocity exists in frame (x,y,z) and is a real velocity in that frame. It vanishes only when there is no rotation i.e. when  $\underline{\omega} = \underline{0}$ . We then have inertial dynamics for which Newton's laws are valid.

#### THE NON INERTIAL ACCELERATIONS

These are generated by operating twice on the r.h.s. of eqn (A1) and (A2) with the appropriate differential operators, giving:

$$\underline{D}_f (\underline{D}_f \underline{r}) \equiv (\underline{D}_m + \underline{\omega x}) [\underline{D}_m + \underline{\omega x}] \underline{r} \quad (\text{A5})$$

and conversely

$$\underline{D}_m (\underline{D}_m \underline{r}) \equiv (\underline{D}_f - \underline{\omega x}) [\underline{D}_f - \underline{\omega x}] \underline{r} \quad (\text{A6})$$

or, in more familiar notation:

$$[\underline{\dot{v}}]_{(x,y,z)} \equiv [\underline{\dot{v}} + 2\underline{\omega x v} + \underline{\dot{\omega} x r} + \underline{\omega x}(\underline{\omega x r})]_{(1,2,3)}, \quad (\text{A7})$$

$$[\underline{\dot{v}}]_{(1,2,3)} \equiv [\underline{\dot{v}} - 2\underline{\omega x v} - \underline{\dot{\omega} x r} + \underline{\omega x}(\underline{\omega x r})]_{(x,y,z)} \quad (\text{A8})$$

Eqn (A8) shows that in non inertial dynamics the Newtonian acceleration  $[\underline{\dot{v}}]_{(x,y,z)}$  is supplemented by three additional non inertial linear accelerations.



Two of these are known by historical development as

- 1) the Coriolis linear acceleration;  $2\omega \times v$  ;
- 2) the centripetal linear acceleration;  $\omega \times (\omega \times r)$  ;

and the third we denote by the "non uniform" linear acceleration;  $-\dot{\omega} \times r$ .

The corollary (eqn. A8) to the frame transformation theorem (eqn. (A7)) shows that the three non inertial linear accelerations exist directly in the laboratory frame  $(x,y,z)$  for  $\dot{\omega} \neq 0$ .

The non inertial linear accelerations may be illustrated with a few examples. The Coriolis acceleration operates on an object moving on the earth's surface because of the rotation of the earth about its axis. The acceleration is in opposite directions in the northern and southern hemispheres. Similarly the linear Newtonian acceleration at instant  $t$  of the centre of mass of a rotating molecule feels a Coriolis acceleration due to the angular velocity of the molecule. One of the ways of perceiving this is to rotate frame  $(1,2,3)'$  at the molecular angular velocity  $\omega$  with respect to the laboratory frame  $(x,y,z)$ . This means that we can view the laboratory frame  $(x,y,z)$  as spinning with respect to the molecule with the same angular velocity. The laboratory frame is therefore a non inertial frame with respect to the translation of the molecule's centre of mass in frame  $(x,y,z)$ . The laboratory frame stops spinning only when the angular velocity is zero taking us back to Newton's original concept. Any Newtonian linear velocity or acceleration in a spinning  $(x,y,z)$  frame must be supplemented by additional terms, the Coriolis linear non inertial acceleration being one of these.

For each molecule in the ensemble there are three non inertial linear accelerations, distributed according to the laws of statistical mechanics. Correlation functions of these accelerations therefore exist in frames  $(x,y,z)$  and  $(1,2,3)$  and are reported elsewhere [5-8].

Note carefully that this type of Coriolis acceleration, present in a rigid molecule that is both rotating and translating, is not the same as the well known Coriolis accelerations which appear in frame  $(x,y,z)$  from the quantum theory of molecules that are vibrating and rotating. In that case the Coriolis acceleration splits infra red spectral lines and is due to a translational motion (bond vibration), superimposed on a rotating frame (that of the rotating molecule's principal molecular moments of inertia for example, or any other (e.g. principal polarisability) frame of reference). The fact that vibration rotation Coriolis quantum effects appear in spectra is proof of the existence of the Coriolis (quantum) acceleration in frame  $(x,y,z)$ . The essential difference between that type and the new type given in this paper is that in vibration rotation the translation in the spinning laboratory frame is due to bond vibration; in centre of mass translation/rotation as in this

("classical") paper, the translation is that of the molecular centre of mass itself.

Finally centripetal acceleration is a real linear acceleration in frame (x,y,z) and can be seen to be so by a static observer in frame (x,y,z) whenever a discus thrower releases the discus. Therefore there is no need to be in a spinning frame of reference to observe the effects of the non inertial accelerations. This is another common misconception. Coriolis splitting in infra red spectra is obviously observed by the spectroscopist in his own static frame (x,y,z).

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