NON-EXPONENTIAL CORRELATION FUNCTION IN DPR: A COMPARISON OF EXPERIMENT AND THE DISTORTED WAVE BORN APPROXIMATION

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The recently observed non-exponential decay of the correlation function for the depolarized Rayleigh (DPR) line in N_2 is examined by a partial calculation of the cross section. The calculation, which is based upon a distorted wave Born approximation (DWBA), shows that the presence of inelastic collisions is necessary to account for the experimental results. Moreover, the inclusion of inelastic collisions has the consequence that the diagonal elements of the relaxation matrix are virtually constant rather than dying off as $[j(j+1)]^{-1}$.

Gas kinetic phenomena are usually interpreted in terms of binary collision rates or effective cross sections [1]. The simplest procedure is to assume that there is only one average collision cross section, or equivalently, one mean free path or free time between collisions. From the point of view of time correlation function theory, this is equivalent to assuming that the time correlation function is exponential. Since experiments actually measure the contributions from many individual molecular states, it is perhaps surprising that this simple approximation works as well as it does.

Measurements of the depolarized Rayleigh line (DPR) in gases show a non-exponential decay of the associated time correlation function [2]. The deviation from exponential decay has been reported in terms of the difference between the cross section $\mathfrak{S}_{\mathrm{DPR}}$ associated with the initial slope and the cross section $\tilde{\mathfrak{S}}_{\mathrm{DPR}}$ associated with the reciprocal of the area under the time correlation function curve [2]. Essentially $\mathfrak{S}_{\mathrm{DPR}}$ measures an average decay rate while $\tilde{\mathfrak{S}}_{\mathrm{DPR}}$ is equivalent to an average decay time. For N_2, the ratio $\tilde{\mathfrak{S}}/\mathfrak{S}$ is 0.92.

For diatomics, the physical observable in DPR is the diagonal-in-j component of the rotational quadrupole moment $[\hat{\mathbf{r}}]^{(2)}_{\mathrm{diag}}$ and experiment is interpreted in terms of the time correlation function

$$F(t) \equiv \frac{\langle\langle [\hat{\mathbf{r}}]^{(2)}_{\mathrm{diag}} | \exp(-\mathcal{R}t) | [\hat{\mathbf{r}}]^{(2)}_{\mathrm{diag}} \rangle\rangle}{\langle\langle [\hat{\mathbf{r}}]^{(2)}_{\mathrm{diag}} | [\hat{\mathbf{r}}]^{(2)}_{\mathrm{diag}} \rangle\rangle} = \frac{\Sigma_{jj'} (p_j)^{1/2} d_j [\exp(-n\langle v\rangle \mathfrak{S} t)]_{jj'} d_{j'} (p_{j'})^{1/2}}{\Sigma_j p_j d_j^2} . \quad (1)$$

Here n is the density, $\langle v\rangle$ the average relative speed of two colliding molecules and $\mathfrak{S}$ is a collision cross section matrix whose components

$$\mathfrak{S}_{jj'} \equiv n^{-1}\langle v\rangle^{-1} \langle\langle 020j | \mathcal{R} | 020j' \rangle\rangle \quad (2)$$

are matrix elements of the Waldmann [3] –Snider [4] collision superoperator $\mathcal{R}$. The notation and inner product are defined in ref. [5]. The Boltzmann probability factors are

$$p_j = (2j+1) \exp[-Bj(j+1)/kT] Q^{-1} , \quad (3)$$

while the expansion coefficients

$$d_j = [j(j+1)/(2j-1)(2j+3)]^{1/2} \quad (4)$$

arise in the expansion

$$[\hat{\mathbf{r}}]^{(2)}_{\mathrm{diag}} = -(\tfrac{2}{15})^{1/2} \sum_j d_j Y^{(2)}(J) P_j$$

$$= -(\tfrac{2}{15})^{1/2} \sum_j d_j (p_j)^{1/2} A_{020j} \quad (5)$$

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of the diagonal-in-j quadrupole moment in terms of the normalized expansion tensors A_{020j}, see ref. [5]. P_j is the projection operator onto the angular momentum magnitude j quantum states. Eq. (1) is equivalent to that of Shafer and Gordon [6] except for the fact that their $\mathfrak{S}$ matrix is not defined in a symmetrical way, so their formula has a compensating asymmetry. It is now immediate that the initial slope of $F(t)$ defines

$$\mathfrak{S}_{\mathrm{DPR}} = \frac{\Sigma_{jj'}(p_j)^{1/2} d_j \mathfrak{S}_{jj'} d_{j'}(p_{j'})^{1/2}}{\Sigma_j p_j d_j^2}, \qquad (6)$$

while the area under the curve gives

$$[\tilde{\mathfrak{S}}_{\mathrm{DPR}}]^{-1} = \frac{\Sigma_{jj'}(p_j)^{1/2} d_j [\mathfrak{S}^{-1}]_{jj'} d_{j'}(p_{j'})^{1/2}}{\Sigma_j p_j d_j^2}. \qquad (7)$$

The latter thus involves the matrix inverse of $\mathfrak{S}$.

A distorted wave Born approximation (DWBA) to the $\mathfrak{S}$ matrix has recently been carried out [7]. For a P_2 potential, which is a reasonable choice for the N_2–N_2 interaction, the formula is

$$\mathfrak{S}_{jj'} = \mathfrak{S}'(020|j|j')$$
$$= 5^{-1/2}\Bigg[\sum_{j''}\left(\frac{p_{j''}}{p_j}\right)^{1/2}\delta_{jj'}[(2j+1)(2j''+1)]^{1/2}$$
$$\times\begin{pmatrix} j & 2 & j'' \\ 0 & 0 & 0\end{pmatrix}^2 \mathfrak{S}_p^{(1)}(00220|00220|\Delta\epsilon_{jj''})$$
$$-(2j+1)(2j'+1)\begin{pmatrix} j & 2 & j' \\ 0 & 0 & 0\end{pmatrix}^2$$
$$\times\begin{Bmatrix} 2 & j & j' \\ 2 & j' & j\end{Bmatrix}\mathfrak{S}_p^{(1)}(00220|00220|\Delta\epsilon_{jj'})\Bigg] \qquad (8)$$

involving 3-j and 6-j symbols. The quantity $\mathfrak{S}_p^{(1)}(\Delta\epsilon)$ arises from an integral over the translational degrees of freedom and depends on the energy inelasticity of the collision.

The ratio of $\tilde{\mathfrak{S}}$ to $\mathfrak{S}$ was calculated for N_2 by Keijser et al. [2] as 0.30 if only energetically elastic collisions occur and the $\mathfrak{S}$ matrix is then given either by setting $j = j' = j''$ in eq. (8) or by eq. (83) of ref. [5]. Of course the $\mathfrak{S}$ matrix is then diagonal and has the interesting feature that for large j, $\mathfrak{S}_{jj}$ behaves as $[j(j+1)]^{-1}$.

In order to investigate the consequence of the inelastic terms, the matrix $\mathfrak{S}$ was evaluated numerically

Table 1

$\tilde{\mathfrak{S}}_{\mathrm{DPR}}/\mathfrak{S}_p^{(1)}(0)$	$\tilde{\mathfrak{S}}_{\mathrm{DPR}}/\mathfrak{S}_p^{(1)}(0)$	$\tilde{\mathfrak{S}}_{\mathrm{DPR}}/\mathfrak{S}_{\mathrm{DPR}}$	γ
0.060	0.030	0.50	1
0.124	0.110	0.89	0.75
0.139	0.128	0.92	0.69
0.254	0.250	0.99	0.25
0.320	0.320	1.00	0
elastic only			
0.0034	0.010	0.30	–

from eq. (8) up to $J = 50$ and the ratio $\tilde{\mathfrak{S}}_{\mathrm{DPR}}/\mathfrak{S}_{\mathrm{DPR}}$ calculated. In doing this it was assumed that the energy inelasticity, $\Delta\epsilon$, was zero so that $\mathfrak{S}_p^{(1)}(0)$ appeared only as a scale factor which cancels in the ratio. This approximation assumes that there is no j dependence of $\mathfrak{S}_p^{(1)}$ and that inelastic and elastic contributions are weighted equally. In this manner the ratio $\tilde{\mathfrak{S}}_{\mathrm{DPR}}/\mathfrak{S}_{\mathrm{DPR}}$ increased to 0.50. As a consequence of the inelastic terms on the diagonal, the elements $\mathfrak{S}_{jj}$ do not behave as $[j(j+1)]^{-1}$ but remain virtually constant.

In order to test the effects of weighting the off-diagonal elements differently from the diagonal ones, a factor γ was introduced so that

$$\gamma = 1 \quad \text{for} \quad j = j';$$
$$= \gamma \quad \text{for} \quad j \neq j'. \qquad (9)$$

It is found that with decreasing γ, the value 0.92 for the ratio is obtained for $\gamma = 0.69$. These results are summarized in table 1. Note that when $\gamma = 0$, the ratio of one indicates that $\mathfrak{S}_{jj}$ is almost independent of j.

Although the introduction of γ is empirical and is in many ways unsatisfactory, it does indicate that additional terms, such as arise from resonance collisions, may be present which compensate the off-diagonal elements more than the diagonal contributions. This is so because γ is not equal to $\mathfrak{S}_p^{(1)}(\Delta\epsilon)/\mathfrak{S}_p^{(1)}(0)$ since then the inelastic *diagonal* terms would be weighted by γ also. If both diagonal and off-diagonal inelastic contributions are weighted by γ, then the ratio of 0.92 cannot be obtained without use of an unreasonably large value of $\mathfrak{S}_p^{(1)}(\Delta\epsilon)/\mathfrak{S}_p^{(1)}(0)$. In actuality, $\mathfrak{S}_p^{(1)}(\Delta\epsilon)$ is j dependent but this has not been investigated here.

The calculation here does demonstrate the impor-

tance of inelastic collision. Moreover it shows that the $[j(j+1)]^{-1}$ behaviour of the diagonal elements is not valid when inelastic collisions are included. Finally it indicates that the DWBA may account for the true non-exponential decay observed in DPR of N_2, but greater knowledge of the non-spherical part of the intermolecular potential and of $\mathfrak{S}_p^{(1)}$ are required for a complete understanding of the experimental results.

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