

# The dipole–octupole contribution to the Rayleigh wings of gaseous nitrogen <sup>☆</sup>

T. Bancewicz, W. Głaz and S. Kielich

*Nonlinear Optics Division, Institute of Physics, Adam Mickiewicz University, Grunwaldzka 6, 60-780 Poznan, Poland*

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The influence of the dipole-induced octupole scattering mechanism on the Rayleigh wings of gaseous nitrogen is considered. Numerical computations for the Rayleigh scattered spectrum are performed. The far wings of the Rayleigh line of gaseous N<sub>2</sub> are shown to be determined almost uniquely by the interaction-induced octupole mechanism of light scattering.

## 1. Introduction

For many years [1], the spectral distribution of the depolarised component of light Rayleigh scattered by systems of molecules with intrinsic optical anisotropy was thought to originate primarily in reorientational rotational motions of molecules of the scattering medium. On discovery of the depolarised component of Rayleigh scattering by systems of optically isotropic molecules forbidden in the single-molecule approximation [2], much attention [3–6] was given to the influence of interactionally induced mechanisms on the Rayleigh spectrum from anisotropic molecules as well.

The first-order dipole-induced dipole (DID) has been found to be the dominant interaction-induced mechanism in fluids of light diatomics [5–11]. However, this mechanism failed to account for the considerable divergences from the value 0.75 of the frequency-dependent depolarisation ratio of the Rayleigh and Raman lines of O<sub>2</sub> [12]. The discrepancy is particularly apparent on the wings.

In the present paper we propose to consider additionally the dipole-induced octupole light scattering mechanism for the interpretation of the far wings of the Rayleigh scattered spectral line. We have performed model numerical computations for the Rayleigh scattered spectrum of gaseous nitrogen, one of the few molecules for which the numerical values of the dipole–octupole polarisability tensor are available [13]. The far wings of the Rayleigh line of gaseous N<sub>2</sub> are shown by us to be determined almost uniquely by the interaction-induced dipole-induced octupole mechanism of light scattering.

## 2. Theory

The spectral distribution of light anisotropically scattered by a fluid is described by the Fourier transform [1]

$$I(\omega) = A_\omega \frac{1}{2\pi} \int dt e^{-i\omega t} C_2(t) \quad (1)$$

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of the autocorrelation function  $C_2(t)$ :

$$C_2(t) = \langle \mathbf{\Pi}_2(0) \odot \mathbf{\Pi}_2(t) \rangle \quad (2)$$

of the anisotropic part  $\mathbf{\Pi}_2$  of the collective polarisability tensor. We shall consider a low density fluid; in this case, the rotational and translational motions of the molecules are treated separately. The autocorrelation function (2) now becomes the product [14,15]

$$C_2(t) = C_2^{\text{rot}}(t) C_2^{\text{tr}}(t) \quad (3)$$

of the rotational  $C_2^{\text{rot}}(t)$  and translational  $C_2^{\text{tr}}(t)$  components and consequently the spectral distribution (1) is the convolution [14]

$$I(\omega) = A_\omega \int I^{\text{rot}}(\omega') I^{\text{tr}}(\omega - \omega') d\omega', \quad (4)$$

where  $I^{\text{rot}}(\omega)$  and  $I^{\text{tr}}(\omega)$  are the Fourier transforms of respectively  $C_2^{\text{rot}}(t)$  and  $C_2^{\text{tr}}(t)$ .

We now proceed to calculate the following model spectrum of Rayleigh scattered radiation (4) under the following assumptions:

- (i) we consider pair correlations only;
- (ii) the molecules in the scattering volume rotate freely in accordance with the predictions of quantum mechanics;
- (iii) we evaluate analytically and numerically the second spectral moment of the translational part of the spectrum and then, applying information theory, we predict the translational spectrum;
- (iv) finally, we calculate the resulting spectrum (4) as the convolution of the rotational and translational spectra.

For fluids, the collective polarisability  $\mathbf{\Pi}_2$  consists of two parts:

$$\mathbf{\Pi}_2 = {}_{(M)}\mathbf{\Pi}_2 + {}_{(DIM)}\mathbf{\Pi}_2, \quad (5)$$

where  ${}_{(M)}\mathbf{\Pi}_2$  is the overall intrinsic molecular polarisability and  ${}_{(DIM)}\mathbf{\Pi}_2$  originates in the interaction-induced dipole-induced multipole mechanisms [4,16–18]. For linear molecules the rotational Rayleigh spectrum resulting from the permanent anisotropy of the molecule has the well known form [19]

$${}^{(ANISO)}I_{VV}(\omega) = \frac{2}{15} N_A A_\omega \frac{\exp(-E_J/kT)}{Z} g_I(2J+1)(2J+1) \begin{pmatrix} J & 2 & J \\ 0 & 0 & 0 \end{pmatrix}^2 |\tilde{A}_{20}^{(11)}|^2 \delta(\omega - \Delta\omega), \quad (6)$$

where

$$E_J = BJ(J+1), \quad \Delta J = J' - J = 0, \mp 2, \quad \Delta\omega = -B [J'(J'+1) - J(J+1)],$$

with the Q ( $\Delta J=0$ ), Stokes S ( $\Delta J=2$ ) and anti-Stokes O ( $\Delta J=-2$ ) branches. In (6),  $\begin{pmatrix} a & b & c \\ 0 & 0 & 0 \end{pmatrix}$  stands for the 3- $j$  Wigner symbol,  $Z$  is the rotational partition function,  $\tilde{A}_{20}^{(11)}$  the irreducible spherical zeroth component of the second-rank part of the Rayleigh polarisability tensor in the molecular frame,  $g_I$  the nuclear-statistical factor, whereas  $\delta(\omega)$  denotes the Dirac delta function. In a first approximation  ${}_{(DIM)}\mathbf{\Pi}_2$  can be expressed in terms of the multipole series expansion [16–18]

$${}_{(DIM)}\mathbf{\Pi}_2 = {}_{(DID)}\mathbf{\Pi}_2 + {}_{(DIQ)}\mathbf{\Pi}_2 + {}_{(DIO)}\mathbf{\Pi}_2 + \dots, \quad (7)$$

where the first term is the dipole-induced dipole (DID) contribution well known from the Yvon–Kirkwood theory, whereas the second and third terms represent, respectively, the dipole-induced quadrupole (DIQ) and dipole-induced octupole (DIO) contributions. For nitrogen, due to the centre of symmetry of the  $N_2$  molecule, the first order DIQ contribution vanishes [18]. Since at present very little is known about the anisotropy of electron-overlap pair polarisabilities of molecular gases (for radial dependence see ref. [20]), we neglect the electron-overlap mechanism. From our preliminary considerations it results that the radial electron-overlap

mechanism does not affect the very far wings of the Rayleigh line which are of main interest here.

When calculating the autocorrelation function (2) as a tensor scalar product one easily notes that the total autocorrelation function is the sum of components of two types: square and cross [18]. Within the quantum free rotor approximation, the cross contributions to the spectral intensity vanish. The square terms of the autocorrelation function (2) due to the dipole-induced multipole (DIM) interaction-induced mechanism have the form

$$\begin{aligned}
 (\text{DIM-DIM}) C_2(t) &= 5N_A \rho \sum_{\substack{R_1 R_2 \\ R'_1 R'_2}} (-1)^{R_1+R'_1} X_{R_1 R_2 R'_1 R'_2} \sum_{\substack{l_1 l_2 R_3 \\ l'_1 l'_2}} \begin{Bmatrix} R_1 & R_2 & R_3 \\ 1 & 1 & 2 \\ l_1 & l_2 & N \end{Bmatrix} \begin{Bmatrix} R'_1 & R'_2 & R_3 \\ 1 & 1 & 2 \\ l'_1 & l'_2 & N \end{Bmatrix} \\
 &\times \langle [\mathbf{A}_{R_1}^{(1l_1)}(1,0) \otimes \mathbf{A}_{R_2}^{(1l_2)}(2,0)]_{R_3} \odot [\mathbf{A}_{R'_1}^{(1l'_1)}(1,t) \otimes \mathbf{A}_{R'_2}^{(1l'_2)}(2,t)]_{R_3} \rangle \\
 &\times \frac{2^N}{[(2l_1!)(2l_2!)(2l'_1!)(2l'_2!)]^{1/2}} \langle \mathbf{T}_N(r_{12}(0)) \odot \mathbf{T}_N(r_{12}(t)) \rangle, \quad (8)
 \end{aligned}$$

where  $X_{ab..f} = [(2a+1)(2b+1) \dots (2f+1)]^{1/2}$ ,  $N_A$  stands for the number of molecules in the scattering volume,  $\rho = N_A/V$ , whereas the remaining notation is that of our previous paper [18]. Within the quantum free rotor approximation the rotational wave function  $\Psi(12)$  for a rotating pair of linear molecules has the following product form [17]:

$$\Psi(12) = \Psi_{J_1 M_1} \Psi_{J_2 M_2} \quad (9)$$

and consequently for  $(\text{DIM-DIM}) I_{VV}^{\text{rot}}(\omega)$  we obtain

$$\begin{aligned}
 (\text{DIM-DIM}) I_{VV}^{\text{rot}}(\omega) &= \frac{4}{3} N_A \rho \sum_{\substack{R_1 R_2 \\ J_1 J_2 J'_1 J'_2}} (-1)^{R_1+R_2} \begin{pmatrix} J'_1 & R_1 & J_1 \\ 0 & 0 & 0 \end{pmatrix}^2 \begin{pmatrix} J_2 & R_2 & J_2 \\ 0 & 0 & 0 \end{pmatrix}^2 X_{J_1 J_2 J'_1 J'_2}^2 \\
 &\times \sum_{\substack{l_1 l_2 \\ l'_1 l'_2}} \begin{bmatrix} 2 & R_1 & R_2 & N \\ 1 & 1 & 1 & l_1 \\ 1 & 1 & 1 & l'_1 \\ 1 & l_2 & 1 & l'_2 \end{bmatrix} \tilde{A}_{R_1 0}^{(1l_1)} \tilde{A}_{R_1 0}^{(1l'_1)} \tilde{A}_{R_2 0}^{(1l_2)} \tilde{A}_{R_2 0}^{(1l'_2)} g_{l_1} g_{l_2} \frac{\exp[-(E_{J_1} + E_{J_2})/kT]}{Z_1 Z_2} \delta(\omega - \Delta\omega), \quad (10)
 \end{aligned}$$

where

$$\begin{bmatrix} a & b & c & d \\ e & f & g & h \\ i & j & k & l \end{bmatrix}$$

is a 12- $j$  symbol of the second kind [21] and

$$\Delta\omega = -B[J_1(J_1+1) + J_2(J_2+1) - J_1(J_1+1) - J_2(J_2+1)].$$

From (10) it results that the interaction-induced part of the rotational intensity  $(\text{DIM-DIM}) I_{VV}^{\text{rot}}(\omega)$  is determined by double rotational transitions [17] occurring simultaneously in molecules 1 and 2. In (10) within the DID mechanism,  $R_1=0$  or 2;  $R_2=0$  or 2, whereas for DIO we have  $R_1=0, 2$ ;  $R_2=2, 4$  (or  $R_1=2, 4$ ;  $R_2=0, 2$ ), implying the following selection rules for  $J_1$  and  $J_2$ :  $\Delta J_1=0, \mp 2$ ;  $\Delta J_2=0, \mp 2, \mp 4$  (or equivalently  $\Delta J_1=0, \mp 2, \mp 4$ ;  $\Delta J_2=0, \mp 2$ ). Thus in addition to the interaction-induced contributions to the above considered Q, S and O branches previously shown to appear in (6) due to the intrinsic molecular anisotropy, we obtain entirely new branches  $\Delta J_1 = \mp 2, \Delta J_2 = \mp 2$  within DID, and moreover  $\Delta J_1 = \mp 2, \Delta J_2 = \mp 2$ ;  $\Delta J_1 = \mp 4, \Delta J_2 = 0$  (or  $\Delta J_1 = 0, \Delta J_2 = \mp 4$ );  $\Delta J_1 = \mp 2, \Delta J_2 = \mp 4$  (or  $\Delta J_1 = \mp 4, \Delta J_2 = \mp 2$ ) originating in the dipole-induced octupole mechanism. The explicit formula for the Stokes side branch  $\Delta J_1 = +2, \Delta J_2 = +4$  is

$$\begin{aligned}
(\text{DIM-DIM})I_{\text{VV}}^{\text{rot}}(\omega) &= \frac{77}{2592} N_A \rho \frac{(J_1+1)(J_1+2)(J_2+1)(J_2+2)}{(2J_1+3)(2J_2+3)} \frac{(J_2+3)(J_2+4)}{(2J_2+5)(2J_2+7)} \\
&\times g_{l_1} g_{l_2} \frac{\exp\{-B[J_1(J_1+1)+J_2(J_2+1)]\}}{Z_1 Z_2} \tilde{A}_{20}^{(11)} \tilde{A}_{20}^{(11)} \tilde{A}_{40}^{(13)} \tilde{A}_{40}^{(13)} \delta(\omega - \Delta\omega), \quad (11)
\end{aligned}$$

where  $\Delta\omega = -2B(2J_1+4J_2+13)$ . Similar relations can be derived from (10) for the remaining interaction-induced rotational branches.

We now proceed to calculate the Fourier transform of the translational part of (8):

$$I_{\text{tr}}^{(N)}(\omega) = \frac{1}{2\pi} \int dt e^{-i\omega t} \frac{2^N}{[(2l_1)!(2l_2)!(2l_1)!(2l_2)!]^{1/2}} \langle T_N(r_{12}(0)) \odot T_N(r_{12}(t)) \rangle. \quad (12)$$

We calculate the translational spectrum for the DID scattering mechanism ( $N=2$ )  $I_{\text{tr}}^{(2)}(\omega)$  as well as for the DIO mechanism of interest here ( $N=4$ )  $I_{\text{tr}}^{(4)}(\omega)$ . We compute the zeroth  $M_0^{(2)}$ ,  $M_0^{(4)}$  and second  $M_2^{(2)}$ ,  $M_2^{(4)}$  moments of (12) for these mechanisms and then, according to information theory [22], maximising the entropy, one can predict the translational spectrum in the form [23]

$$I_{\text{tr}}^{(2)}(\omega) = 3M_0^{(2)} (\lambda^{(2)}/\pi)^{1/2} \exp(-\lambda^{(2)}\omega^2), \quad (13a)$$

$$I_{\text{tr}}^{(4)}(\omega) = 7M_0^{(4)} (\lambda^{(4)}/\pi)^{1/2} \exp(-\lambda^{(4)}\omega^2), \quad (13b)$$

where

$$\lambda^{(l)} = M_0^{(l)}/2M_2^{(l)}.$$

Calculating the above moments we obtain the following translational parts of the spectrum:

$$I_{\text{tr}}^{(2)}(\omega) = 6 \left( \frac{\beta m_{12}}{60\pi} \right)^{1/2} \langle r_{12}^{-6} \rangle \left( \frac{\langle r_{12}^{-6} \rangle}{\langle r_{12}^{-8} \rangle} \right)^{1/2} \exp(-\lambda^{(2)}\omega^2), \quad (14a)$$

$$I_{\text{tr}}^{(4)}(\omega) = 28 \left( \frac{\beta m_{12}}{180\pi} \right)^{1/2} \langle r_{12}^{-10} \rangle \left( \frac{\langle r_{12}^{-10} \rangle}{\langle r_{12}^{-12} \rangle} \right)^{1/2} \exp(-\lambda^{(4)}\omega^2), \quad (14b)$$

where  $\beta = 1/kT$ ,  $m_{12}$  is the reduced mass of the  $\text{N}_2$  molecule, and the mean values  $\langle r_{12}^{-n} \rangle$  are defined as

$$\langle r_{12}^{-n} \rangle = 4\pi \int r_{12}^{-n+2} \exp(-\beta U_{12}) dr_{12} d\omega_1 d\omega_2 / \int d\omega_1 d\omega_2, \quad (15)$$

where  $\omega_1$  and  $\omega_2$  denote the orientation of molecule 1 and 2 respectively. We consider the potential  $U_{12}$  as resulting from two-site Lennard-Jones as well as quadrupole-quadrupole interactions [9]:

$$U_{12}(r_{12}, \omega_1, \omega_2) = 4\epsilon \sum_{a,b=1}^2 [(\sigma/r_{ab})^{12} - (\sigma/r_{ab})^6] + U_{\text{QQ}}, \quad (16)$$

with  $\epsilon/k = 36.4$  K,  $\sigma = 3.318$  Å,  $a = 0.55$  and  $Q = -1.15$  DA. Then for molecular parameters  $\langle r_{12}^{-n} \rangle$  we obtain  $\langle r_{12}^{-6} \rangle = 0.124$  Å<sup>-3</sup>,  $\langle r_{12}^{-8} \rangle = 6.48 \times 10^{-3}$  Å<sup>-5</sup>,  $\langle r_{12}^{-10} \rangle = 3.98 \times 10^{-4}$  Å<sup>-7</sup>,  $\langle r_{12}^{-12} \rangle = 2.33 \times 10^{-5}$  Å<sup>-9</sup>.

### 3. Numerical computations, and conclusions

Finally, we calculate numerically the convolution (4) of the rotational (10) and translational (14) parts of the spectrum. The resulting spectrum is shown in fig. 1, where we have plotted separately the contributions due to the permanent anisotropy, the DID interaction-induced scattering mechanism, as well as that due to

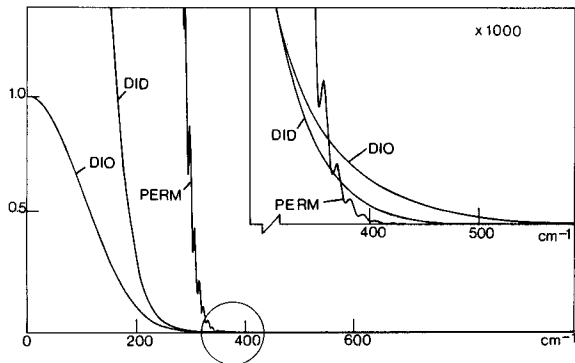


Fig. 1. The contributions to the Rayleigh spectrum of gaseous nitrogen ( $T=300$  K,  $\rho=1$  amagat) due to the permanent anisotropy, DID and DIO interaction-induced scattering mechanisms (Stokes side). The Q branch of the permanent anisotropy spectrum is not indicated here. The upper right corner inset spectrum represents the far wing part of the spectrum encircled on the main graph. See the text for discussion.

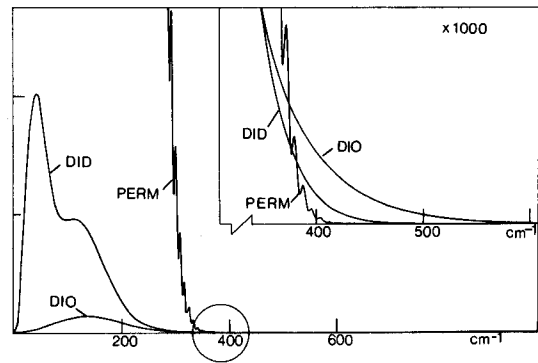


Fig. 2. The contributions to the second moment-generating function  $\omega^2 I(\omega)$  of the Rayleigh spectrum of gaseous  $N_2$  (Stokes side) due to the permanent anisotropy, DID and DIO interaction-induced scattering mechanisms. The upper inset represents the far wing part of the generating function encircled on the main picture.

the DIO mechanism of main interest here. To take into account the influence of the aperture slit on the spectrum we have broadened our theoretical spectrum with a Gaussian function having a full width of  $3.6 \text{ cm}^{-1}$  at half maximum. Moreover we have normalised our spectra to the DIO  $\omega=0$  value. From the main graph of fig. 1 it results that starting from about  $150 \text{ cm}^{-1}$  the DID and DIO contributions to the net Rayleigh spectrum of gaseous nitrogen are comparable, but both these contributions are overshadowed by the spectrum due to the permanent anisotropy of  $N_2$ . The upper right corner inset spectrum represents the far wings part of our spectrum (upward of  $400 \text{ cm}^{-1}$ ) encircled on the main picture. The intensity here has been multiplied by 1000. In this spectral region the permanent anisotropy spectrum rapidly decreases to zero whereas the DID and DIO mechanism still give contributions to the net spectrum. At the far wings the DIO spectrum intersects the DID spectrum and determines the major contribution to the net spectrum. The DID spectrum decreases faster than the DIO one and roughly above  $500 \text{ cm}^{-1}$ , DIO subsists as the only mechanism responsible for the far wings of our model spectrum of gaseous  $N_2$ .

Since the DIO interaction-induced scattering mechanism contributes significantly at the far wings of the  $N_2$  spectrum we have examined the spectral moments in our search for the influence of the DIO mechanism on the generating function  $\omega^n I(\omega)$  for these moments. Fig. 2 shows that the DIO mechanism is more strongly pronounced within the function  $\omega^2 I(\omega)$  generating the second moment than within the original spectrum of fig. 1.

Our theoretical and computational results prove the significance of the dipole-induced octupole interaction-induced scattering mechanism for the explanation of the Rayleigh far wings of gaseous nitrogen. Since the interaction-induced signal is linear in density, eqs. (8)–(11), we are able to enhance the induced contributions to the spectrum as compared with that from the permanent anisotropy by raising the density. We have performed the above numerical computations for 1 amagat but believe that, within our model, the density might be raised roughly up to 20 amagats. Further calculations of the isotropic spectrum of  $N_2$  and the frequency dependent depolarisation ratio of the Rayleigh spectral line, as well as experimental work, are in progress [24].

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