## 4. TITLE AND SUBTITLE

Depolarization ratio of Rayleigh scattered radiation by molecules

## 6. AUTHORS

Ramesh D. Sharma
Kelly D. Burtt* 

## 7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Air Force Research Laboratory /VSBYB  
29 Randolph Road  
Hanscom AFB, MA 01731-3010

## 8. PERFORMING ORGANIZATION REPORT NUMBER

AFRL-VS-HA-TR-2007-1029

## 9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

AFRLNSBYB

## 10. SPONSOR/MONITOR'S ACRONYM(S)

AFRL/VSBYB

## 11. SPONSOR/MONITOR'S REPORT NUMBER(S)


## 12. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for Public Release; distribution unlimited.

## 13. SUPPLEMENTARY NOTES

*Institute for Scientific Research, Boston College, Chestnut Hill, MA 02467

## 14. ABSTRACT

The depolarization ratios of Rayleigh scattered radiation by molecules has been used to measure the ratio of anisotropic polarizability in the laboratory. The authors have calculated the depolarization ratio for N₂, CH₃Cl, and H₂O from the first principles. It is shown that the depolarization ratio derived from input polarizabilities differs by a factor of about 4 for "Σ diatom N₂", by a factor of about 2.9 for symmetric top CH₃Cl, and by a factor of about 5 for asymmetric top H₂O. These large discrepancies arise because in deriving the ratio of anisotropic polarizability to isotropic (average) polarizability from the measured depolarization ratio, the constraints imposed by the conservation of angular momentum have been completely ignored.

## 15. SUBJECT TERMS

Rayleigh scattering Angular distribution Polarization vector Depolarization ratio

## 16. SECURITY CLASSIFICATION OF:

a. REPORT UNCL  
b. ABSTRACT UNCL  
c. THIS PAGE UNCL  

## 17. LIMITATION OF ABSTRACT

UNL

## 18. NUMBER OF PAGES

1

## 19. NAME OF RESPONSIBLE PERSON

Ramesh D. Sharma

## 19B. TELEPHONE NUMBER

(Include area code)
Depolarization ratio of Rayleigh scattered radiation by molecules

Ramesh D. Sharma and Kelly D. Burtt
Space Vehicles Directorate/VSBYM, Hanscom Air Force Base, Massachusetts 01731-3010
pp. 024306 1-6
Depolarization ratio of Rayleigh scattered radiation by molecules

Ramesh D. Sharma and Kelly D. Burtt
Space Vehicles Directorate/VSBYM, Hanscom Air Force Base, Massachusetts 01731-3010

(Received 19 October 2006; accepted 17 November 2006; published online 12 January 2007)

The depolarization ratios of Rayleigh scattered radiation by molecules has been used to measure the ratio of anisotropic polarizability to isotropic (average) polarizability in the laboratory. The authors have calculated the depolarization ratio for $N_2$, $CH_3CI$, and $H_2O$ from the first principles. It is shown that the depolarization ratio derived from input polarizabilities differs by a factor of about 4 for $^1\Sigma$ diatom $N_2$, by a factor of about 2.9 for symmetric top $CH_3CI$, and by a factor of about 5 for asymmetric top $H_2O$. These large discrepancies arise because in deriving the ratio of anisotropic polarizability to isotropic (average) polarizability from the measured depolarization ratio, the constraints imposed by the conservation of angular momentum have been completely ignored.

\[ I_1(\alpha,j_i,j_f) = \frac{\chi_{o,0}^\alpha}{(2\alpha+1)} C^2(j,\alpha j_f;0,0), \]
\[ I_2(\alpha) = \sum_q \sum_{\epsilon M, \phi_\epsilon} E_{\epsilon q} \left( \frac{\pi}{2}, \phi_\epsilon \right) E_{\epsilon M, \phi_\epsilon} \left( \frac{\pi}{2}, \phi_\epsilon \right) d_\epsilon^{1/2} C(11\alpha; M, q-M)^2, \]
\[ \chi_{o0} = C(110; 00)\alpha_{zz} - C(110; 1,-1)(\alpha_{xx} + \alpha_{yy}) = -\left( \frac{1}{3} \right)^{1/2} (\alpha_{zz} + \alpha_{xx} + \alpha_{yy}) = -\left( \frac{3}{2} \right)^{1/2} \alpha_{av}, \]
\[ \chi_{2,0} = C(112; 00)\alpha_{zz} - C(112; 1,-1)(\alpha_{yy} + \alpha_{xx}) = \left( \frac{2}{3} \right)^{1/2} (\alpha_{zz} - \frac{1}{2}(\alpha_{xx} + \alpha_{yy})) = \left( \frac{2}{3} \right)^{1/2} \gamma, \]
\[ \chi_{2,\pm2} = \left( \frac{3}{8} \right)^{1/2} C(112; \pm 1, \pm 1)(\alpha_{xx} - \alpha_{yy} \pm 2i\alpha_{xy}). \]

INTRODUCTION

In a recent article, Sharma\textsuperscript{1} has shown that the contribution of polarizability anisotropy to Rayleigh scattering given in literature by molecules is valid only for diatoms and only in the high temperature (high rotational quantum number) limit. It was also shown that this error is introduced by approximating the constraint imposed by the conservation of angular momentum to be 1/4, the high temperature value of the vector coupling coefficients. The introduced error has the opposite sign for $N_2$ and $O_2$, two important molecules. The magnitude of the calculated error monotonically decreased as the frequency of the incident radiation, $\omega$, is increased; for $N_2$ it decreased from 4% to 2% while for $O_2$ it decreased from -11% to -5% as the temperature increased from 100 to 300 K. Since the measurement of depolarization ratio\textsuperscript{2,3} is used to arrive at the ratio of anisotropic polarizability to isotropic (average) polarizability, it was considered advisable to calculate this error for molecules. In this article we have calculated the depolarization ratio of the Rayleigh scattered radiation for three molecules, a simple $^1\Sigma$ diatomic ($N_2$), a symmetric top (CH3Cl), and an asymmetric top (H2O), and compared the calculated values with the measured ones. We show that the neglect of constraints imposed by the conservation of angular momentum overestimates the ratio of anisotropic polarizability to isotropic (average) polarizability by a factor of about 2 for $N_2$, about 1.7 for CH3Cl, and about 2.2 for H2O.

FORMULATION

The differential cross section for Rayleigh scattering through angle $\beta$ by a $^1\Sigma$ diatomic molecule ($N_2$) is given by the expression

\[ \frac{d\sigma}{d\Omega}(\beta) = \frac{\omega_0^3}{c^2} \sum_{\alpha} I_1(\alpha,j_i,j_f) \times I_2(\alpha), \]

with

\[ I_1(\alpha,j_i,j_f) = \frac{\chi_{o,0}^\alpha}{(2\alpha+1)} C^2(j,\alpha j_f;0,0), \]
\[ I_2(\alpha) = \sum_q \sum_{\epsilon M, \phi_\epsilon} E_{\epsilon q} \left( \frac{\pi}{2}, \phi_\epsilon \right) E_{\epsilon M, \phi_\epsilon} \left( \frac{\pi}{2}, \phi_\epsilon \right) d_\epsilon^{1/2} C(11\alpha; M, q-M)^2, \]
\[ \chi_{o0} = C(110; 00)\alpha_{zz} - C(110; 1,-1)(\alpha_{xx} + \alpha_{yy}) = -\left( \frac{1}{3} \right)^{1/2} (\alpha_{zz} + \alpha_{xx} + \alpha_{yy}) = -\left( \frac{3}{2} \right)^{1/2} \alpha_{av}, \]
\[ \chi_{2,0} = C(112; 00)\alpha_{zz} - C(112; 1,-1)(\alpha_{yy} + \alpha_{xx}) = \left( \frac{2}{3} \right)^{1/2} (\alpha_{zz} - \frac{1}{2}(\alpha_{xx} + \alpha_{yy})) = \left( \frac{2}{3} \right)^{1/2} \gamma, \]
\[ \chi_{2,\pm2} = \left( \frac{3}{8} \right)^{1/2} C(112; \pm 1, \pm 1)(\alpha_{xx} - \alpha_{yy} \pm 2i\alpha_{xy}). \]

The change in magnetic quantum number (projection of the angular momentum of the molecule on the space-fixed axis) of the molecule in Eq. (3) is represented by $q$. C in Eqs. (2)--(6) is the Clebsch-Gordan (vector coupling) coefficient; $C^2(j,\alpha j_f;0,0)$ ensures the conservation of angular momentum. The conservation of angular momentum also requires that the differences in the projections of the electric vectors of the incident and scattered photons on a space-fixed $z$ axis
equal \( q \); this is ensured by the Clebsch-Gordan coefficient 
\[ C(11\alpha; M, q-M), \]
\( M \) being the projection of the electric vector of the incident photon and \( q-M \) being the projection of the electric vector of the scattered photon on the space-fixed \( z \) axis. The plane containing the incident and scattered photons, the scattering plane, is the \( xz \) plane of the space-fixed coordinate system. The incident and the scattered photons travel along the \( z \) axis of the coordinate systems fixed in the incident and scattered beams; these two coordinate systems share a common \( y \) axis perpendicular to the scattering plane (Fig. 1). The space-fixed coordinate system is taken to be the one fixed in the incident beam. The \( e_M \) and \( e_p \) are projections of the electric vectors of the incident and scattered photons on the spherical coordinate systems embedded in the respective beams and \( d^l_{p,q;k}(\beta) \) is the rotation matrix of order 1 that transforms the projection \( p \) to \( q-M \), its projection on the space-fixed coordinate system (incident beam), via rotation by the scattering angle \( \beta \) around the \( y \) axis common to the two beams.

When extending Eq. (1) to polyatomic molecules two complications arise.

1. A \( ^1\Sigma \) diatomic molecule rotates with its plane of rotation perpendicular to its angular momentum vector. The projection of the angular momentum vector on the internuclear axis \( k \), a good quantum number, is zero. The wave function of the molecule in the rotational level \( j \) is given by
\[ |j, k=0, m\rangle=[2j+1/8\pi^2]^{1/2}D^j_{m,0}(\Omega), \]
where \( m \) is the magnetic quantum number (projection of the angular momentum vector on the space-fixed axis) and \( D \) is the rotation matrix\(^5\) of order \( j \). A \( ^1\Sigma \) polyatomic molecule with an \( n \)-fold axis of symmetry \( (n \geq 3) \) has two equal moments of inertia (symmetric rotor), e.g., \( CH_2Cl \), and rotates with its plane of rotation at a fixed angle to its angular momentum vector. The projection of the angular momentum vector on the axis of symmetry of the molecule \( k \) is no longer a good quantum number. The rotational wave function of the molecule in the rotational level \( j \) is now given by a linear combination of those of a symmetric rotor with a suitably chosen axis of symmetry for the molecule (for \( H_2O \) along the dipole moment),
\[ |j, m, \pm\rangle=\sum_{k'}a_{k'}|j, k', m, \pm\rangle, \]
where \( k' \) takes even or odd non-negative integral values up to \( j \) and \( \pm \) refers to the parity of the suitably normalized symmetric rotor wave functions upon changing \( k' \) to \(-k' \), \( \tau \) being the index that has \( (2j+1) \) values from \(-j \) to \( j \) and orders the wave functions according to energy—the larger the energy, the higher the value of \( \tau \). We constructed the rotational wave functions at the rigid rotor level of approximation following Zare\(^2\) and Dennison and Hecht\(^3\).
TABLE I. Six sets of values of the three polarizabilities (in Å³) taken from the literature and $\alpha_{xx}$, $\beta$, $\chi_{x0}$ and $\chi_{x2}$ derived from them. The data sets with references are A (Ref. 8), B (Ref. 9), C (Ref. 10), D (Ref. 11), E (Ref. 12), and F (Ref. 3).

<table>
<thead>
<tr>
<th>Data set</th>
<th>$\alpha_{xx}$</th>
<th>$\alpha_{yy}$</th>
<th>$\alpha_{zz}$</th>
<th>$\alpha_{xy}$</th>
<th>$\beta$</th>
<th>$\chi_{x0}$</th>
<th>$\chi_{x2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1.503</td>
<td>1.431</td>
<td>1.451</td>
<td>1.417</td>
<td>0.004</td>
<td>-0.130</td>
<td>0.044</td>
</tr>
<tr>
<td>B</td>
<td>1.651</td>
<td>1.226</td>
<td>1.452</td>
<td>1.443</td>
<td>0.135</td>
<td>0.011</td>
<td>0.260</td>
</tr>
<tr>
<td>C</td>
<td>1.696</td>
<td>1.221</td>
<td>1.519</td>
<td>1.4787</td>
<td>0.172</td>
<td>0.049</td>
<td>0.290</td>
</tr>
<tr>
<td>D</td>
<td>1.850</td>
<td>1.350</td>
<td>1.480</td>
<td>1.560</td>
<td>0.201</td>
<td>-0.097</td>
<td>0.306</td>
</tr>
<tr>
<td>E</td>
<td>1.765</td>
<td>1.360</td>
<td>1.590</td>
<td>1.5417</td>
<td>0.123</td>
<td>0.022</td>
<td>0.248</td>
</tr>
<tr>
<td>F</td>
<td>1.5284</td>
<td>1.4146</td>
<td>1.4679</td>
<td>1.4703</td>
<td>0.009</td>
<td>-0.029</td>
<td>0.069</td>
</tr>
</tbody>
</table>

\( \rho_n = \frac{I_\parallel}{I_\perp} = \frac{6\gamma^2}{180(\alpha_{xy})^2 + 7\gamma^2}, \)  \hspace{1cm} (12c)

which approximates \( C^2(j2;00) = j(j+1)/(2j-1)(2j+3) \) by 1/4, independent of \( j \), and hence of temperature, as well as of the molecular species involved. The earlier literature has completely ignored these constraints and has given \( \rho_n \) and \( \rho_0 \) by Eqs. (12a) and (12b) omitting \( C^2(j2;00) \) and overestimating the depolarization ratio by about a factor of 4 for \( 1\Sigma \) diatoms. Alternatively from a measured value of the depolarization ratio the derived \( \gamma/\alpha_{xy} \) is an overestimate by a factor of about 2 for \( 1\Sigma \) diatoms. As pointed out earlier there is negligible error involved in approximating the vector coupling coefficient \( C^2(j2;00) \) by 1/4 for \( N_2 \) at 300 K. Taking \( \gamma = 0.691 \text{ Å}^3 \text{ from Asawaroengchai and Rosenblatt}^{14} \) and \( \alpha_{xy} = 1.738 \text{ Å}^3 \text{ from Zeiss and Meath}^{15} \) we obtain \( \rho_0 = 2.6 \times 10^{-3} \) 1/4 times the measured value of \( (0.96 \pm 0.14) \times 10^{-2} \) by Murphy at room temperature. The depolarization ratio for a symmetric top, a function of \( j \) and \( |k| \), is given by

\( \rho_{nc}(j,|k|) = \frac{I_\perp}{I_\parallel}, \)  \hspace{1cm} (13)

with

\( I_\perp = \frac{2\gamma^2}{15} \left[ (3k^2 - j(j+1))^2 \right] \) \hspace{1cm} (13a)

and

\( I_\parallel = (\alpha_{xy})^2 + \frac{72\gamma^2}{6} \left[ (3k^2 - j(j+1))^2 \right]/15 \left[ (j(j+1)(2j-1)(2j+3)) \right]. \) \hspace{1cm} (13b)

Assuming that the energy of interaction of the nuclear spins with the rotational motion is much smaller than the width of the laser beam used to measure the depolarization ratio (Appendix), Fig. 3 gives a plot of \( \rho_{nc}/\rho_n \) for CH₂Cl as a function of temperature. Even though the value of \( \rho_{nc}/\rho_n \) is a strong function of \( k \) it shows little variation as a function of temperature, remaining about 0.72 over the 100–300 K temperature range. Taking the values of \( \alpha_{xy} \) and \( \gamma \) from Bridge and Buckingham and those of rotational constants from Herzberg we get \( \rho_0 = 1.4 \times 10^{-3} \). The measured value of the depolarization ratio by Bridge and Buckingham at room temperature is \( 7.66 \times 10^{-3} \). This value is close to the value \( \rho_{nc}(4/0.72) = 7.78 \times 10^{-3} \) one would get by ignoring the constraints imposed by the conservation of angular momentum.

The differential cross section for Rayleigh scattering by an asymmetric rotor is given by Eq. (1) with

\( \rho_n = \frac{I_\parallel}{I_\perp} = \frac{6\gamma^2}{180(\alpha_{xy})^2 + 7\gamma^2}, \)  \hspace{1cm} (12c)

where \( \rho_n \) is the depolarization ratio.

\( \beta = \frac{1}{2}[(\alpha_{zz} - \alpha_{xx})^2 + (\alpha_{yy} - \alpha_{xy})^2 + (\alpha_{xx} - \alpha_{yy})^2] \)

This expression reduces to Eq. (3) when \( \alpha_{xy} = \alpha_{xx} = \alpha_{yy} = 0 \) and \( \alpha_{xx} = \alpha_{yy} \) for H₂O only the former holds and

\( \beta = \frac{1}{2}[(\alpha_{zz} - \alpha_{xx})^2 + (\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{xy})^2] \)

\( = \gamma^2 + (\chi_{2.3})^2 + (\chi_{2.2})^2, \)  \hspace{1cm} (11)

with \( \gamma = (\alpha_{zz} - 1/2)(\alpha_{yy} + \alpha_{xx}) \) and \( \chi_{2,2} = \chi_{x2} \)

It is at once seen that when the magnitude of anisotropy is used to derive the depolarization ratio, any constraints imposed by the conservation of angular momentum are absent. Table I gives six sets of values of the three polarizabilities in Å³ taken from the literature and \( \alpha_{xy}, \beta, \chi_{x0}, \) and \( \chi_{x2} \) derived from them. The polarizabilities given here take the z axis along the symmetry axis of the molecule (axis with intermediate moment of inertia) and the y axis perpendicular to the plane of the molecule (axis with the greatest moment of inertia).

If the incident beam travels along the z axis (polarization vector along the y axis or y axis) and the scattered radiation is observed along the x axis (polarization vector along the z axis or y axis), as shown in Fig. 1, the depolarization ratio \( \rho \) is defined as the ratio of the intensity of light with polarization vector rotated by 90° (polarization vector along the y axis or z axis), \( I_1 \), to the intensity of light with unchanged polarization vector (polarization vector along the z axis or y axis), \( I_0 \). Sharma has shown that for unpolarized (natural) light the contribution of \( I_2(\alpha=2) \), Eq. (3), to \( I_1 \) is unity while its contribution to \( I_0 \) is 7/6. For unpolarized (natural) light the calculated depolarization ratio \( \rho_{nc} \) for \( N_2 \) is then given by

\( \rho_{nc}(j) = \frac{I_\perp}{I_\parallel} = \frac{6\gamma^2 C^2(j2;00)}{45(\alpha_{xy})^2 + 7\gamma^2 C^2(j2;00)} \) \hspace{1cm} (12a)

For the polarized light the contribution of \( I_2(\alpha=2) \), Eq. (3), to \( I_\perp \) is 1/2 while its contribution to \( I_\parallel \) is 2/3. The depolarization ratio then becomes

\( \rho_{nc}(j) = \frac{I_\perp}{I_\parallel} = \frac{3\gamma^2 C^2(j2;00)}{45(\alpha_{xy})^2 + 4\gamma^2 C^2(j2;00)} \) \hspace{1cm} (12b)

The value of \( \rho_n \) given in literature is 13
To calculate $I_1(j,\alpha=2)$ we have computed the rotational wave functions for the ground vibrational state of H$_2$O at the rigid rotor level of approximation. We now calculate $\rho_{nc}$ assuming that (Appendix) the energy of interaction of the nuclear spins with the rotational motion is much smaller than the width of the laser beam used to measure the depolarization ratio ($\sim$1 MHz). A plot of $\rho_{nc}/\rho_n$ as a function of $j_\tau$ (with $\tau$ increasing from left to right for each $j$) for $j=1$–9 is shown in Fig. 4; the value for $j=0$ being identically equal to zero is not shown. Although this ratio approaches 3–4, depending on the values of the polarizabilities used, for the lowest and highest values of $\tau$ as $j$ approaches nine, it remains close to zero independent of $j$ for middle values of $\tau$, just as it approaches zero for the value of $|k|$ halfway between 0 and $j$ for symmetric tops. Figure 5 gives a plot of $\rho_{nc}/\rho_n$ as a function of temperature for the six sets of the polarizability data. The six data sets divide into two groups; the ratio of $\rho_{nc}/\rho_n$ for the first group (data sets B, C, E, and F) decreases from about 1.32 to about 1.27 while for the second group (data sets A and D) it decreases from about 1.24 to about 1.18 as the temperature increases from 150 to 300 K. The $\rho_{nc}/\rho_n$ ratio for either set, just as the corresponding one for symmetric top CH$_3$Cl, does not approach unity even at 300 K. Taking $\rho_{nc}/\rho_n=1.25$ at 300 K we get, using the value for the polarizabilities given by Murphy$^3$, $\rho_{nc}=0.94\times10^{-4}$. The measured value of the depolarization ratio by Murphy$^3$ at room temperature is $2.99\times10^{-4}$, close to the value $\rho_{nc}(4/1.25)=3.01\times10^{-4}$ one would get by ignoring the constraints imposed by the conservation of angular momentum.

CONCLUSION

The ratio of the calculated depolarization ratio to that given in literature, $\rho_{nc}/\rho_n$, for symmetric tops shows great variation with $|k|$ for a given value of $j$. However, for symmetric top CH$_3$Cl it shows little variation as a function of temperature, remaining about 0.72 over the 100–300 K temperature range. The ratio $\rho_{nc}/\rho_n$ for asymmetric top water vapor also shows large variation with $\tau$ for a given value of $j$. However, it also shows little variation as a function of temperature and decreases from 1.32 (1.24) at 150 K to 1.27 (1.18) at 300 K. The ratio $\rho_{nc}/\rho_n$ does not approach unity either for the symmetric top or the asymmetric top even at 300 K.

Bridge and Buckingham$^2$ have measured depolarization ratio $\rho_{BBB}=3\gamma^2/45\alpha_w^2+4\gamma^2$ of polarized light from a helium-neon gas laser by CH$_3$Cl at room temperature to be $7.66\times10^{-3}$. This expression can, with accuracy better than 0.5%, be approximated as $\rho_{BBB}=\gamma^2/15\alpha_w^2$. The ratio $(\gamma/\alpha)^2$ derived by these authors from the measured depolarization
ratio is an overestimate by $4 \times 0.72 = 2.88$, the overestimate of the ratio of anisotropic to average (isotropic) polarizability ($\gamma/\alpha$) being about 1.7.

By the same arguments the ratio of anisotropic to average (isotropic) polarizability of water vapor is overestimated by about 2.2.

This underscores the fact that the contribution of the polarizability anisotropy to Rayleigh scattering by molecules is not correctly described in the literature.

ACKNOWLEDGMENTS

The authors are grateful to Professor Richard N. Zare for suggesting improvements in the manuscript. This research was performed while K. D. B. held a National Research Council Research Post-doctoral Associate Award at the Air Force Research Laboratory.

APPENDIX: NUCLEAR SPIN AND RAYLEIGH SCATTERING

The two nuclei of the hydrogen atoms in H$_2$O each have spin 1/2, and are therefore fermions; the O atom has zero nuclear spin and is therefore a boson. The total nuclear spin of the two protons is zero (antisymmetric; degeneracy 1) or 1 (symmetric; degeneracy 3).

The ground state electronic and vibrational wave functions of H$_2$O are symmetric (do not change sign) upon interchanging the two H atoms. Therefore the product of the rotational wave function and nuclear spin wave function of H$_2$O has to be antisymmetric upon interchanging the two H atoms.

Para rotational wave functions (++ or -- symmetry) which do not change sign upon interchange of two H atoms must have an antisymmetric (total nuclear spin zero) nuclear wave function. These levels are unaffected by nuclear spin considerations.

Ortho rotational wave functions (+- or -- symmetry) which change sign upon interchange of two H atoms must have symmetric (total nuclear spin one) nuclear wave function. The combined rotational $(j,\alpha)$ nuclear spin ($S_N$) wave function for the initial and final states can be written as

$$|JM_S;S_N\rangle = \sum_{m_1} C(j,S_N,\alpha;M-m_1,m_1)|j,M-m_1\rangle|S_N,m_1\rangle,$$

(A1)

$$|J'M'_S;S_N\rangle = \sum_{m_1} C(j,S_N,\alpha;M'-m_1,m_1)|j,M'-m_1\rangle|S_N,m_1\rangle.$$

(A2)

The function $I_1$ [Eq. (2)] for an asymmetric rotor becomes

$$I_1(j,\alpha) = \sum_{k,k',x,m_1} C(j,S_N,\alpha;M-m_1,m_1)C(j',S_N;M')$$

$$\times \delta(k,k')\delta(x,x)C(j,\alpha;\kappa,k)\frac{\alpha}{\kappa} \left| \sum_{k,k',\kappa} X_{x,\kappa}\alpha_{k'}\alpha_{k}\langle C(j,\alpha;\kappa,k)\delta(k,k')\rangle^2 \right|^2.$$ 

(A3)

We now write, defining $\kappa = M'-M$, 

$$C(j',S_N;M+q-m_1,m_1)$$

$$= (-1)^{j'-M-\frac{q}{2}+m_1} \left( \frac{2j'+1}{2S+1} \right)^{1/2}$$

$$\times C(j',S_N;M+q-m_1,m_1-M-q)$$

$$= (-1)^{j'+M+q}\left( \frac{2j'+1}{2S+1} \right)^{1/2}$$

$$\times C(j',S_N;M-q,M+q-m_1).$$

(A4)

$$C(j,S_N;M-m_1,m_1) = C(S_N,j;M-m_1,m_1-M).$$

(A5)

Using the relation

$$\sum_{m_1} C(j',S_N;M-M-q,M+q-m_1)C(S_N,j;M-m_1,M_1-M)$$

$$\times C(j',j;M+q-m_1,m_1-M)$$

$$= [(2\alpha+1)(2S_N+1)]^{1/2} W(j',j;\alpha;S_N\alpha)$$

$$\times C(j,j;M-M-q)$$

$$= (-1)^{j'+M+q}(2j'+1)(2S+1)^{1/2} W(j',j;\alpha;S_N\alpha)$$

$$\times C(j,j;M-M-q),$$

(A7)

we get

$$I_1(j,\alpha) = \frac{(2j'+1)(2j+1)}{(2\alpha+1)} W(j',j;\alpha;S_N\alpha)$$

$$\times \left| \sum_{k,k',\kappa} X_{x,\kappa}\alpha_{k'}\alpha_{k}\langle C(j,\alpha;\kappa,k)\delta(k,k')\rangle^2 \right|^2.$$ 

(A8)

This expression is very similar to the one for Rayleigh scattering from O$_2(\Sigma)$ molecule.
(2N 1)(2J + 1)

\[ I_1(N,J,J',S;\alpha)_{\alpha_2} = \frac{(2N + 1)(2J + 1)}{(2\alpha + 1)} \times C^2(NaN;00)W^2(JN\alpha;S\alpha), \]

(A9)

where \( N \) and \( J \) are the initial and final rotational and total angular momenta, \( S=1 \) is the electron spin, and \( \alpha=2 \) is the rank of the polarizability tensor.

If we assume that the coupling of the nuclear spin with molecular rotation leading to splitting of the rotational levels is much smaller than either the linewidth of the rotational levels or the width of the laser line (~1 MHz) used to determine the depolarization ratio, we can then assume \( j_r=j'_r \) and sum Eq. (8) over \( J \). Using the relations

\[ W^2(J',J;j_r,S\alpha) = W^2(j_rS\alpha;J',J'), \]

(A10)

\[ \sum_{J} (2J+1)(2j_r+1)W^2(j_rS\alpha;J';J) = 1, \]

(A11)

we get

\[ I_1(j_r,\alpha) = \frac{1}{(2\alpha + 1)} \left| \sum_{k_i,k_f,\kappa} \chi_{\alpha,\alpha} a_{k_i}^* a_{k_f} C(j_r,\alpha;j_r;k_i,\kappa) - \kappa, k_f \right| \delta_{k_i,k_f,\kappa} \right|^2. \]

(A12)

Finally recalling that for each value of \( j_r \), there are \((2S_N+1)\) values of \( J' \) and summing over these values, we get

\[ I_1(j_r,\alpha) = \frac{(2S_N+1)}{(2\alpha + 1)} \left| \sum_{k_i,k_f,\kappa} \chi_{\alpha,\alpha} a_{k_i}^* a_{k_f} C(j_r,\alpha;j_r;k_i,\kappa) - \kappa, k_f \right|^2. \]

(A13)