### ABSTRACT

[1] Differential cross sections for Raman scattering between the multiplet levels of the ground electronic state of atomic oxygen are calculated from first principles. The calculated cross sections are in order-of-magnitude agreement with the available experimental measurements. The use of a Raman LIDAR (Light Detection and Ranging) has the potential of giving a three-dimensional map of the density of each of the three fine structure levels of atomic oxygen. Since it was established earlier that the fine structure levels are in local thermodynamic equilibrium (LTE) up to at least 350 km altitude, the Raman LIDAR therefore also has the potential of giving a three-dimensional map of the temperature of the atmosphere.

### SUBJECT TERMS

Atomic oxygen  
Raman transitions  
Raman LIDAR  
Thermodynamic equilibrium  
Atmospheric temperature

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[1] Differential cross sections for Raman scattering between the multiplet levels of the ground electronic state of atomic oxygen are calculated from first principles. The calculated cross sections are in order-of-magnitude agreement with the available experimental measurements. The use of a Raman LIDAR (Light Detection and Ranging) has the potential of giving a three-dimensional map of the density of each of the three fine structure levels of atomic oxygen. Since it was established earlier that the fine structure levels are in local thermodynamic equilibrium (LTE) up to at least 350 km altitude, the Raman LIDAR therefore also has the potential of giving a three-dimensional map of the temperature of the atmosphere.

INDEX TERMS: 0310 Atmospheric Composition and Structure: Thermosphere—composition and chemistry; 0340 Atmospheric Composition and Structure: Middle atmosphere—composition and chemistry; 0342 Atmospheric Composition and Structure: Middle atmosphere—energy deposition; KEYWORDS: atomic oxygen, Raman transitions between fine structure levels, Raman LIDAR, local thermodynamic equilibrium, three-dimensional map of atmospheric temperature and atomic oxygen density


1. Introduction

[2] The role of atomic oxygen in the heat budget of the terrestrial thermosphere can hardly be overestimated [Sharma and Roble, 2002]. Three important processes involving atomic oxygen, namely the 15 μm emission pumped by the impacts of O with CO₂, 5.3 μm emission pumped by the impacts of O with NO, and 63 μm fine-structure emission O(3P₁) → O(3P₂) are the dominant mechanisms for cooling the thermosphere and determining its temperature and density structure [Sharma and Roble, 2001]. It is therefore very desirable to know the temperature and density of atomic oxygen in the thermosphere. Recent satellite-based passive remote sensing of atomic oxygen density in the 130–175 km altitude range by measuring the 63 μm limb emission by Cryogenic Infrared Spectrometers and Telescopes (CRISTA) aboard ASTRO-SPAS (Astronomical Shuttle Pallet Satellite) for the November 1994 to August 1997 period [Grossmann et al., 2000] have given very surprising results: “The resultant densities are on the average about 40% below the predictions of the MSIS model for the low solar activity conditions of the CRISTA experiments and at all altitudes covered by the measurement. The densities exhibit considerable horizontal structures which are only in partial agreement with the MSIS predicted variations. The latitudinal distribution shows steeper decreases towards the poles than given in MSIS.”

[3] The CRISTA measurements, while showing considerable horizontal structure, also, because they are limb measurements, average the structure over the line-of-sight and partially mask it. Since it is possible to gate the scattered Raman pulse, one can determine the O density and temperature in a particular space-time interval, giving us a method of determining these two very important parameters for atmospheric modeling without limb averaging over a couple of thousand kilometers. It is hoped that this work will be as useful to future experiments as our previous work [Sharma et al., 1988, 1990, 1994; Zachor and Sharma, 1989] was to CRISTA experiments. Assuming the fine structure levels of atomic oxygen to be in local thermodynamic equilibrium (LTE), Sharma et al. [1988] showed that the 63 μm and 145 μm transitions could be inverted in the 90–250 km altitude range. The simulated signal with noise incorporated was inverted in the 145 μm channel by Zachor and Sharma [1989] and in the 63 μm channel by Sharma et al. [1990]. Since the idea that the fine structure levels were in LTE was not generally accepted, the newly calculated cross sections for transitions between the fine structure levels during O-O impacts [Zygelman et al., 1994a, 1994b] were used to demonstrate that these levels were always in LTE at least up to 350 km altitude [Sharma et al., 1994].

[4] Atoms with half-filled or completely filled outer electronic orbit have only isotropic polarizability and therefore do not Raman shift the frequency of the incident radiation. Atoms with neither half-filled nor completely filled outer electronic orbit, on the other hand, possess both isotropic and anisotropic polarizabilities and therefore do Raman shift the frequency of the incident radiation. From these considerations, Schlossberg [1976] pointed out that the fluorine atoms might be detected by monitoring the Raman scattered radiation and estimated
that about $10^{16}$ atoms could be detected by this method. The atomic oxygen ground electronic state ($^3\text{P}$) has eight electrons $1s^22s^22p^4$ and its outer electronic orbit is neither half-filled nor completely filled. It therefore has nonzero anisotropy of polarizability; hence Raman scatters incident radiation. Dasch and Bechtel [1981] measured, with an excitation source of 532.1 nm, the Raman scattering cross section without change in polarization of ground state atomic oxygen. These authors also calculated the Raman scattering cross section assuming that the $^3\text{S}_1$ electronic state located at 76,700 cm$^{-1}$ is the only state that makes a significant contribution to the Raman cross section. Since Dasch and Bechtel [1981] do not give details of their calculation, and since the transition moment, derived by us in Appendix A, differs by a factor of 1.4 from that given by these authors, we repeat their calculation using the full power of the angular momentum algebra [Zare, 1987]. We obtain results that are in order-of-magnitude agreement with the available measurements.

Section 2 gives the formulation of the equations; the results are computed and compared with the earlier measurement and calculation of Dasch and Bechtel in section 3. Section 4 states the possible application of these results to measuring the atomic oxygen density and temperature in the terrestrial thermosphere.

2. Formulation

The transition probability for going from state $a$ to state $b$ with the absorption of a photon of frequency $\omega$ from the electromagnetic field and the emission of one of frequency $\omega_0$ in solid angle $d\Omega$ is given by Fermi's Golden Rule [Kramers, 1964]

$$ P = \frac{2\pi}{\hbar} \int d\omega |\langle b|W(\omega, t)|a\rangle|^2 \delta(\omega_0 - \omega) \rho(\omega) d\Omega. \quad (1) $$

where $\rho(\omega)$ is the density of states per unit frequency interval. $W(\omega, t)$ is the interaction energy of the electromagnetic field of frequency $\omega$, and a spinless particle of mass $\mu$, momentum $p$, and charge $e$ given by

$$ W(\omega, t) = -\frac{e}{\mu c}(\lambda_p + \frac{e^2}{2\mu c^2} A^2) \quad (2) $$

$$ A(\omega, t) = e \left( \frac{2\pi \hbar}{\omega} \right)^{1/2} e^{i\omega t} \left( e^{ik\cdot r} + e^{-ik\cdot r} \right). \quad (3) $$

The electromagnetic field is normalized to contain one photon of frequency $\omega$ in unit volume and $e$ is a unit (polarization) vector in the direction of the electric field perpendicular to the propagation vector $k$ of the radiation. The density of states $\rho(\omega)$ of the electromagnetic field per unit frequency interval per unit volume in solid angle $d\Omega$ is given by

$$ \frac{d\rho(\omega)}{d\omega} = \frac{\omega^2}{(2\pi)^3} d\Omega. \quad (4) $$

It is usual in the literature to incorporate an additional factor of two in equation (4), corresponding to the two independent polarization directions of the emitted photon. Since we calculate the scattering cross section for the two directions of polarization separately, our density of states will not have that additional factor of two.

We make the dipole approximation and assume that the dimensions of the atoms and molecules we are dealing with are very short compared to the wavelength of the electromagnetic radiation and approximate $\exp(i\mathbf{k}\cdot\mathbf{r})$ term in equation (3) by unity. Using the relationship between the expectation values of the momentum and dipole operators

$$ \langle n|p|m \rangle = i\hbar \omega \langle n|\mu|m \rangle, \quad (5) $$

where

$$ \omega_{\text{hom}} = \left( \frac{E_n - E_m}{\hbar} \right) $$

is the transition frequency between levels $n$ and $m$. We can now write the first-order matrix elements of the interaction operator $W$ between states $n$ and $m$

$$ \langle n|W|m \rangle = -i\hbar \omega \left( \frac{2\pi \hbar}{\omega} \right)^{1/2} e^{i\mu_{\text{hom}} e^{i\omega t} \left( e^{ik\cdot r} + e^{-ik\cdot r} \right)}. \quad (6) $$

Raleigh and Raman scattering are second-order processes, i.e., in going from the initial state $a$ to final state $b$ the interaction operator acts twice. The second-order interaction operator consists of three terms: (1) An incident photon of frequency $\omega$ is absorbed and the particle (atom or molecule) undergoes a transition to virtual state $|v\rangle$ followed by the emission of a photon of frequency $\omega_0$ with the particle going to the final state $|f\rangle$. (2) A photon of frequency $\omega_0$ is emitted and the particle undergoes a transition to virtual state $|v\rangle$ followed by absorption of a photon of frequency $\omega$ with the particle going to the final state $|f\rangle$. (3) A photon of frequency $\omega$ is simultaneously emitted and absorbed and the particle stays in the initial state.

The first two terms are called the Kramers-Heisenberg terms while the third one is called the Waller term [Mizushima, 1970]. The Waller term is also called the $A^2$ term because it arises due to this interaction in the perturbation potential (equation (2)). An interesting point deserves mention here: The atom acts purely as a spectator in the Waller or the $A^2$ term, i.e., undergoing no change at all. This term, although 4-5 orders of magnitude smaller [Loudon, 1983], is still needed to obtain the commonly given expression for Rayleigh and Raman scattering given below (equation (7)).
The three terms summed together give the differential cross section for scattering photons [Mizushima, 1970; Kramers, 1964; Sharma and Levin, 1973]:

$$\frac{d\sigma}{d\Omega} = \frac{\omega^2}{\pi} \left| \sum_n \left( \frac{\langle f | (e, \mu) | \psi \rangle \langle \psi | e, \mu | i \rangle}{(E_n - E_i - \hbar \omega)} + \frac{\langle f | (e, \mu) | \psi \rangle \langle \psi | e, \mu | i \rangle}{(E_n - E_i + \hbar \omega)} \right) \right|^2$$

where

- \(\hbar \omega\) is the energy of the incident photon.
- \(\hbar \omega\) is the energy of the scattered photon.
- \(|i\rangle\) is the wavefunction of the initial state of the particle.
- \(|\psi\rangle\) is the wavefunction of the virtual state of the particle.
- \(|f\rangle\) is the wavefunction of the final state of the particle.
- \(e\) is the dipole moment operator.
- \(e_\circ\) is the polarization (electric) vector of the incident photon.
- \(e_\circ\) is the polarization (electric) vector of the scattered photon.

We now write [Zare, 1987]

$$e, \mu = \sum_{M=-1}^{1} e_{M} Y_{M}(\mathbf{\Omega})_v$$

where \(e_{M} \) are the projections of the vector \(e\) on the unit vectors along the \((1/2)^{1/2}(x - iy), -1 \times (2)^{1/2}(x + iy)\) axes, respectively. The projection \(e_{M} \) corresponds to left (right) circular polarization. Radiation polarized along x-axis is obtained by the coherent (summing before taking absolute square) combination \((1/2)^{1/2}(x - iy)\) while that polarized along y-axis is represented coherently by the combination \((1/2)^{1/2}(x + iy)\). Recalling that \(\frac{4\pi}{3}\mu Y_{1m}(\mathbf{\Omega})_v\) we can write

$$e, \mu = \left(\frac{4\pi}{3}\right)^{1/2} \mu \sum_{M=-1}^{1} e_{M} Y_{M}(\mathbf{\Omega})_v$$

Similarly, we can write

$$\epsilon, \mu = \left(\frac{4\pi}{3}\right)^{1/2} \mu \sum_{M=-1}^{1} \epsilon_{M} Y_{M}(\mathbf{\Omega})_v$$

To derive the scattering angle and polarization dependence of the emitted radiation, we follow Sharma and Levin [1973] and consider two coordinate systems: one fixed in the incident beam (coordinate system 1) and the other fixed in the scattered beam (coordinate system 2). We take the y-axes of the two beams along their respective directions of propagation. The z-axis of the two coordinate systems is taken perpendicular to the plane containing the incident and scattered beams. The two coordinate systems thus have the same z-axis and, in the experimental setup of Dasch and Bechtel [1981], coordinate system 1 can be transformed into coordinate system 2 by a 90° counter clockwise rotation about this axis. Further, the incident beam is polarized along the z-axis. Thus we are restricted to \(M = 0\) in Equation 9 to only one value, \(M = 0\). Further, without loss of generality, we can pick our space-fixed coordinate system to be coincident with the coordinate system 2.

The ground state of atomic oxygen is \(3P_j, j = 1, 2, 3\). The different \(j\) levels are split because of the spin-orbit interaction with \(3P_j\) being the lowest at 0 cm\(^{-1}\), \(3P_1\) at 158.2687 cm\(^{-1}\), and \(3P_0\) at 226.9851 cm\(^{-1}\) [Zink et al., 1991]. Using the Wigner-Eckart theorem, the matrix element of \(e, \mu\) between the initial and virtual states can be written [Zare, 1987]

$$\langle n'' | e | n' \rangle = \left(\frac{4\pi}{3}\right)^{1/2} \left(\frac{n'' | e | n'|}{(2j'' + 1)(2j' + 1)} \right)^{1/2} W(j'' e''; s') \times (\ell'' || Y_1 || \ell)C(j^n_{f''}; m; 0, m)\delta_{m''m'}$$

and the matrix element in the uncoupled representation

$$\langle \ell'' || Y_1 || \ell \rangle = C(1\ell''; 00) \left[ \frac{3(2j'' + 1)}{4(2j'' + 1)} \right]$$

giving

$$\langle n'' | e | n' \rangle = \left(\frac{n'' | e | n'|}{(2j'' + 1)(2j' + 1)} \right)^{1/2} W(j'' e''; s') \times C(j^n_{f''}; m; 0, m)\delta_{m''m'}$$

where \(\langle n'' | e | n' \rangle\) is the radial matrix element of the dipole moment \(e,\mu\). The Clebsch-Gordan coefficients, and \(W\) is the Racah coefficient. The third "magnetic or M" quantum number in a Clebsch-Gordan coefficient is equal to the sum of the first two and is omitted when there is no danger of confusion. The matrix element of \(e,\mu\) between the virtual and final states can be similarly written as

$$\langle n'' | e | n' \rangle = \left(\frac{n'' | e | n'|}{(2j'' + 1)(2j' + 1)} \right)^{1/2} W_{n''}^{m''}(e_j | e_j'; m'' - q) \times C(j^n_{f''}; m; 0, m)\delta_{m''m'}$$

$$\times (-1)^jC(j^n_{f''}; m; 0, m)\delta_{m''m'}$$

and

$$C(j^n_{f''}; m; 0, m) = (-1)^j \left(\frac{2j'' + 1}{2j' + 1}\right)^{1/2} C(j^n_{f''}; m; -q, m - q)$$

[10] The ground state of atomic oxygen is \(3P_j, j = 1, 2, 3\). The different \(j\) levels are split because of the spin-orbit interaction with \(3P_j\) being the lowest at 0 cm\(^{-1}\), \(3P_1\) at 158.2687 cm\(^{-1}\), and \(3P_0\) at 226.9851 cm\(^{-1}\) [Zink et al., 1991]. Using the Wigner-Eckart theorem, the matrix element of \(e, \mu\) between the initial and virtual states can be written [Zare, 1987]
we can write
\[
\langle f | (e' \hat{r}) | k \rangle = \langle n' | e' \hat{r} d \langle n' | e' \hat{r} | n \rangle \delta_{\epsilon_0} \delta_{\epsilon_0'} c_{m'}
\]
\[
\times (-1)^{s_{\epsilon} s_{\epsilon'} - s_{\epsilon_0} s_{\epsilon_0'}} m' \begin{pmatrix}
(2j + 1) & (2j' + 1)
\end{pmatrix}
\]
\[
\times (2j' + 1)(2j'' + 1)(2j' + 1) \right] C(\ell \ell'; 000)
\]
\[
\times C(\ell \ell'; 000) W(\ell j'' j'; s'' | s'') W(j'' j'; s'' | s) x(-1)^{s_{\epsilon} s_{\epsilon'} - s_{\epsilon_0} s_{\epsilon_0'}} m' \begin{pmatrix}
(2j + 1) & (2j' + 1)
\end{pmatrix}
\]
\[
\times (2j' + 1)(2j'' + 1)(2j' + 1) \right] C(j'' j'; m, -m + q, q)
\]
\[
\times C(11f; 0, -q, -q) W(j 1j'; j' f)
\]
(17)

Averaging over the initial magnetic quantum numbers \(m\) and summing over the final ones for a given value of \(q\) we get
\[
\frac{d\sigma}{d\Omega} (j \rightarrow j') = \frac{\omega_{0j}^2}{c^2} \sum_{q} (2j + 1) C(11f; 0, -q, -q) [c_{q}]^2
\]
\[
\times \left[ \begin{pmatrix}
(E_v - E_i - h\omega) & (E_v - E_f + h\omega)
\end{pmatrix}
\right]
\]
\[
\times C(\ell \ell'; 000) C(\ell \ell'; 000)
\]
\[
\times W(j' j'' j'; s'' | s) W(j' j'' j'; s'' | s) W(j 1j'; j' f)
\]
(18)

In equation (18) \(f\) denotes the rank of the polarizability tensor and \(q\) denotes the direction of the polarization vector of the scattered photon.

### 3. Computation of Raman Scattering Cross Sections

[13] Equation (18) is used to calculate Raman Scattering cross sections between the multiplet components of atomic oxygen with different \(j\) values. The Kronecker deltas require that the virtual states must also be spin triplets. Also, \(\ell = \ell' = s = s' = 1\). For the Racah coefficient \(W(j' j'' j'; f)\) with \(j \neq j'\) to be nonzero, the index \(f\) must be nonzero. Therefore only anisotropic components of the polarizability tensor can Raman scatter between the multiplets of the ground state of atomic oxygen. Following Dasch and Bechtel [1981], we assume that only one virtual state, the \(^3S_1\) state \((76700 \text{ cm}^{-1})\), makes a significant contribution to the scattering process. Noting that \(\ell'' = 0\) and \(j'' = 1\) gives \(W(1j0; 1) = W(1j1; 1) = 1/3\). We also note that \(\ell = \ell' = 1\), giving \(C(10; 00) = -(1/3)^{1/2}\) and \(C(01; 00) = 1\). Substituting these values as well as the dipole moments from Appendix A, we get
\[
\frac{d\sigma}{d\Omega} (j \rightarrow j') = \frac{\omega_{0j}^2}{c^2} (1.2 \times 10^{-18})^4 \sum_{q} (2j' + 1) C(11f; 0, -q, -q) [c_{q}]^2
\]
\[
\times \left[ \begin{pmatrix}
(E_v - E_i - h\omega) & (E_v - E_f + h\omega)
\end{pmatrix}
\right]
\]
\[
\times C(1j; 1f) W(j 1j'; j' f)
\]
(19)

If the scattered radiation has the same polarization as the incident beam, i.e., it is polarized in the z direction, then \(q = 0, c_{-q} = 1,\) and \(f = 0, 2\). Since \(f\) has to be nonzero for transition from one multiplet level to another, only \(f = 2\) is allowed. The combination \(j = 1, j' = 0,\) and \(f = 2\) does not satisfy the triangular inequality leading to the Racah coefficient \(W(110; 12) = 0\); thus the transition \(^3P_1 \rightarrow ^3P_0\), shifted 68.7165 cm\(^{-1}\) from the incident frequency, without change in the direction of the polarization vector is not Raman allowed. The differential cross section for Raman scattering from multiplet level \(j\) to level \(j'\) without change in the polarization is then
\[
\frac{d\sigma}{d\Omega} (j \rightarrow j') = \frac{\omega_{0j}^2}{c^2} (1.2 \times 10^{-18})^4 \sum_{q} (2j' + 1) C^2(112; 00, 00)
\]
\[
\times \left( \begin{pmatrix}
(E_v - E_i - h\omega) & (E_v - E_f + h\omega)
\end{pmatrix}
\right)
\]
\[
\times W(j 1j'; 12)
\]
(20)

For the incident radiation of 532.1 nm wavelength, the differential cross section for the \(^3P_0 \rightarrow ^3P_1\) Raman transition is \((2.0 \times 10^{-31}) \text{ cm}^2/\text{str}\) and that for the \(^3P_1 \rightarrow ^3P_2\) Raman transition is \((1.5 \times 10^{-31}) \text{ cm}^2/\text{str}\); the ratio of the two cross sections is just the ratio of the squares of the Racah coefficients
\[
\frac{W(112; 12)}{W(012; 12)} = \frac{3}{4}
\]

The experimentally measured cross sections are \((4 \pm 1) \times 10^{-31}\) and \((6 \pm 1) \times 10^{-31} \text{ cm}^2/\text{str}\), respectively. The calculation of Dasch and Bechtel [1981] gives \((1.2 \times 10^{-31}) \text{ cm}^2/\text{str}\) for \(^3P_0 \rightarrow ^3P_1\) and \((2.8 \times 10^{-31}) \text{ cm}^2/\text{str}\) for \(^3P_1 \rightarrow ^3P_2\). The ratio of the cross sections calculated by us \(= 0.75\) while that obtained by Dasch and Bechtel is 2.3; the experimental ratio being 1.5 ± 0.6.

[14] The expression for the differential cross section for Raman scattering with change in the direction of polarization is
\[
\frac{d\sigma}{d\Omega} (j \rightarrow j') = \frac{\omega_{0j}^2}{c^2} (1.2 \times 10^{-18})^4 \sum_{q} \sum_{\ell, q} (2j' + 1)
\]
\[
\times \left( \begin{pmatrix}
(E_v - E_i - h\omega) & (E_v - E_f + h\omega)
\end{pmatrix}
\right)
\]
\[
\times W(j 1j'; 1f)
\]
(21)

For the x direction of the polarization vector of the scattered photon, \(q = \pm 1\) and \([c_{-q}]^2 = [c_{q}]^2 = 1/2\). Using \(C(111; 01) = C(111; 01) = C(112; 01) = C(112; 01) = 1/2\), we can write the expression for the differential cross section as
\[
\frac{d\sigma}{d\Omega} (j \rightarrow j') = \frac{\omega_{0j}^2}{c^2} (1.2 \times 10^{-18})^4 \sum_{q} \sum_{\ell, q} (2j' + 1)
\]
\[
\times \left( \begin{pmatrix}
(E_v - E_i - h\omega) & (E_v - E_f + h\omega)
\end{pmatrix}
\right)
\]
\[
\times W(j 1j'; 1f)
\]
(22)
The \( f = 1 \) term gives zero for the differential cross section of the \( ^3P_0 \rightarrow ^3P_2 \) transition, since \( W(0121;11) = 0 \). The differential cross section of the \( ^3P_0 \rightarrow ^3P_1 \) Raman transition, which is zero when the polarization is unchanged, is \( 1.5 \times 10^{-31} \text{ cm}^2/\text{str} \). The cross section for the \( ^3P_1 \rightarrow ^3P_2 \) transition is \( 0.6 \times 10^{-31} \text{ cm}^2/\text{str} \).

Using the relations

\[
(n'\ell' \parallel Y_1 \parallel n\ell) = C(\ell\ell';00) \left[ \frac{3(2\ell + 1)}{4\pi(2\ell' + 1)} \right] \]  

and

\[
C(jj'; m, M, m + M) = (-1)^{j'-m} \left( \frac{2j' + 1}{3} \right) \times C(jj'; m, -m - M, -M), \]

we get

\[
|e \cdot \langle n'\ell'^Jj'\parallel m'|n'\ell'\parallel sj| \rangle|^2 = C^2(\ell\ell';00) \left[ \frac{2(2\ell + 1)(2\ell' + 1)}{3} \right] \times W^2((j\ell'j'; s1)|(n'\ell'\parallel m'|\ell')^2 \]  

Taking the absolute square, averaging over the initial magnetic quantum number, and summing over the final ones and over \( M \) also, we get

\[
|e \cdot \langle t's't'\parallel m'|t| \rangle|^2 = C^2(\ell\ell';00) \left[ \frac{2(2\ell + 1)(2\ell' + 1)}{3} \right] \times W^2((j\ell'j'; s1)|(n'\ell'\parallel m'|\ell')^2 \]

where we have written \( \omega_n = \omega \) and \( e \) is the polarization vector of the emitted photon and \( \mu \) is the dipole moment operator. Anticipating that the absolute square of the matrix element will be shown to be angle independent, we integrate over the solid angle obtaining

\[
P = \tau^{-1} = \frac{2}{\hbar^2} \int d\omega |\langle n|\hat{W}(\omega, t)|m|\rangle|^2 \epsilon \cdot (b|\mu|a)^2. \]

Without loss of generality we take our space-fixed \( z \)-axis along the direction of propagation of the emitted photon. Using the Wigner-Eckart theorem, we obtain

\[
e \cdot \langle n'\ell's'j'm'\parallel n'\ell'\parallel sjm \rangle = \left( \frac{4\pi}{3} \right)^{\frac{1}{2}} (2j' + 1)(2j + 1) \times W((j\ell'j'; s1)|(n'\ell'\parallel Y_1 \parallel m'\ell')\parallel n'\ell'\parallel m|) \sum_{M=-1}^{+1} \epsilon \cdot \mu C(jj'; m, M, m') \]  

Using the relations

\[
(n'\ell' \parallel Y_1 \parallel n\ell) = C(\ell\ell';00) \left[ \frac{3(2\ell + 1)}{4\pi(2\ell' + 1)} \right] \]  

and

\[
C(jj'; m, M, m + M) = (-1)^{j-m} \left( \frac{2j + 1}{3} \right) \times C(jj'; m, -m - M, -M), \]

we get

\[
|e \cdot \langle t's't'\parallel m'|t| \rangle|^2 = C^2(\ell\ell';00) \left[ \frac{2(2\ell + 1)(2\ell' + 1)}{3} \right] \times W^2((j\ell'j'; s1)|(n'\ell'\parallel m'|\ell')^2 \]

To evaluate the radial integral from the radiative lifetime of the \( ^3S_1 \rightarrow ^3P_2, J = 0,1,2 \), we start with Fermi's Golden rule

\[
P = \tau^{-1} = \frac{2\pi}{\hbar^2} \int d\omega |\langle b|\hat{W}(\omega, t)|a \rangle|^2 \epsilon \cdot (\omega_n - \omega) \rho(\omega) d\Omega, \]

where \( \tau = 4.8 \text{ ns} \) [Wiese et al., 1966] is the radiative lifetime of the \( ^3S_1 \rightarrow ^3P_2 \) transitions at 76,700 cm\(^{-1}\), and the matrix element is the transition dipole moment between the upper and lower level. Proceeding as in section 2, we can write

\[
P = \tau^{-1} = \frac{1}{2\pi\hbar} \left( \frac{\omega_n}{c} \right)^2 \int d\Omega |\epsilon \cdot (\mu|\mu|a)^2|, \]

\[\text{Table 1a. Differential Cross Section (cm}^2/\text{str}) \text{ Raman Scattering for 532.1 nm Radiation (x10}^{-31}\text{) Without Change of Polarization} \]

<table>
<thead>
<tr>
<th>Transition</th>
<th>Frequency Shift, cm(^{-1})</th>
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<tr>
<td>(^3P_0 \rightarrow ^3P_2)</td>
<td>226.9851</td>
<td>2.0</td>
<td>1.2</td>
</tr>
<tr>
<td>(^3P_1 \rightarrow ^3P_2)</td>
<td>158.2686</td>
<td>1.5</td>
<td>2.8</td>
</tr>
<tr>
<td>(^3P_0 \rightarrow ^3P_1)</td>
<td>68.7165</td>
<td>0.0</td>
<td>0.0</td>
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</tbody>
</table>

The \( f = 2 \) term gives zero for the differential cross section of the \( ^3P_0 \rightarrow ^3P_1 \) transition because \( W(0111;12) = 0 \). The cross sections for the \( ^3P_1 \rightarrow ^3P_2 \) and \( ^3P_0 \rightarrow ^3P_1 \) Raman scattering with \( z \) to \( x \) change of polarization are \( 1.5 \times 10^{-31} \) and \( 1.7 \times 10^{-31} \) cm\(^2/\text{str}\), respectively. The cross sections for Raman scattering with \( z \) to \( x \) change of polarization are \( 1.5 \times 10^{-31}, 1.5 \times 10^{-31} \), and \( 1.7 \times 10^{-31} \) cm\(^2/\text{str}\) for the \( ^3P_0 \rightarrow ^3P_2, ^3P_0 \rightarrow ^3P_1, \) and \( ^3P_1 \rightarrow ^3P_2 \) transitions, respectively. These results are summarized in Tables 1a and 1b.
Recalling that the initial state is $^2S_1$, i.e., $s = 1, l = 0, \text{ and } j = 1$, and
final state is $^2P_{3/2}$, i.e., $s' = 1, l' = 1, \text{ and summing over } j' = 0, 1, 2, (C^2(011;00) = 1 \text{ and } W^2(011;j';11) = 1/9),$ we get

$$|e \cdot (n'|\mu|n)|^2 = \frac{2}{27} \sum_{j} (2j' + 1) |(n'|\mu|n)|^2.$$  \hfill (A9)

Substituting in equation (A3), we get the equation for the radiative lifetime

$$P = \tau^{-1} = \frac{4}{2\pi h} \left(\frac{c}{c}^3\right) \sum_{j} (2j' + 1) |(n'|\mu|n)|^2 \frac{4}{2h} \left(\frac{c}{c}^3\right) \sum_{j} (2j' + 1) = \frac{4}{3h} \left(\frac{c}{c}^3\right) |(n'|\mu|n)|^2.$$

\hfill (A10)

giving $|(n'|\mu|n)|^2 = 1.2 \times 10^{-18}$ esu-cm. Dasch and Bechtel [1981] obtain a value of $1.7 \times 10^{-18}$ esu-cm for this matrix element, a value larger by a factor of 1.4 than that calculated here.

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