CHAPTER II

ULTRAVIOLET RAMAN SCATTERING THEORY

2.1 Raman Frequencies and Transition Strengths

Raman scattering occurs through weak inelastic interactions of light with electronic, vibrational, or rotational transitions of matter. These inelastic interactions induce an energy exchange between the incident light (photon) and the scattering matter, which is typically a molecular gas. The incident light and scattering molecule is considered as a system whose energy must be conserved before, during, and after the scattering process. An additional constraint, the photon hypothesis, states that light energy is grouped into discrete quanta, or photons, with the energy, \( E \), of each photon given by the product of Planck’s constant, \( h \), and the frequency of the photon, \( \nu \), according to \( E = h \nu \). To satisfy the law of conservation of energy and the photon nature of light, the scattered light’s energy can only differ from the energy of the incident photon by discrete n-tuple values of the scattering molecule’s internal energy according to \( \Delta E = n \cdot h \nu \) where \( n = 0,1,2,… \) and \( \nu \) is molecule’s fundamental vibrational frequency. Scattering transitions in which the scattered photon energies are less than or greater than the energy of the incident photons are designated as Stokes and anti-Stokes transitions, respectively. The Stokes, \( \nu_S \), and anti-Stokes, \( \nu_{AS} \), frequencies, in terms of wavenumbers (cm\(^{-1}\)), are described quantum mechanically by:

\[
\nu_S = (\nu_o - \Delta E/hc) = (\nu_o - \nu_{nm}) \tag{2-1}
\]

\[
\nu_{AS} = (\nu_o + \Delta E/hc) = (\nu_o + \nu_{nm}) \tag{2-2}
\]

where \( \nu_o \) is the incident light/laser frequency, \( c \) is the speed of light, and \( \Delta E \) is the energy difference between the final and initial states of the scattering molecule, or \( \nu_{n_e-m} \). Therefore for a sample of molecules, the observed spectral shifts (\( \Delta E \)) of the resulting radiation are the electronic, vibrational, and rotational frequencies of the internal molecular energy levels and the relative intensities/scattering strengths of the shifts provide a direct measure of the total population of molecular energy levels for the sampled molecules. In contrast to the weak inelastic light scattering processes, Rayleigh scattering is an elastic light scattering process in which the molecule retains its initial energy; no frequency shift occurs between incident and
emitted photons yielding more efficient scattering. The Stokes and anti-Stokes Raman scattering processes along with Rayleigh scattering are shown schematically in Fig. 2-1.

A complete derivation of the Raman scattering process must involve a quantum mechanical treatment of the interaction of the incident radiation with the scattering molecule. The scattering system is defined by Schrödinger’s equation, \( i\hbar \frac{\partial}{\partial t} \Psi = \hat{H} \Psi \), where \( \hat{H} \) is the time-dependent Hamiltonian containing the inter/intra-molecular potentials (i.e., kinetic and potential energy terms), \( E \) represents the internal molecular energy structure, and with the state of the molecule completely defined by an appropriate wave function, \( \Psi \). The incident light, which is an electromagnetic wave, is treated as an oscillating electric field that perturbs the molecular system or more specifically the charge distribution of the molecule’s electron cloud. This perturbation results in an induced oscillating polarization of the molecule and promotes transitions between molecular energy levels. The corresponding solution to the time-dependent Schrödinger equation, the eigenfunctions of the perturbed wave functions, indicate the change in energy from the initial to the final state (i.e. the frequency shift, \( \nu_{nm} \)) and the scattering strength of the transition. A complete derivation of the quantum mechanical basis for Raman scattering is beyond the scope of this work; therefore, the proceeding discussion will highlight the working equations for Raman scattering that result from the quantum solution. First, the energy structure of the molecular system will be defined and then followed by a concise explanation of the induced polarizability that produces the scattering process. Lastly, the equations for the scattered Raman intensities will be given based on the molecular energy structure and induced polarizability. A more complete quantum mechanic and classical explanation of the Raman scattering process can be found in Placzek (1934), Steele (1971), and Long (1977).

The overall wave function, \( \Psi \), that describes the state of the molecule is expressed as the product of the normal modes of molecular motion:

\[
\Psi = \Psi_e \Psi_t \Psi_v \Psi_J \Psi_n
\]  

(2-3)

where \( e, t, v, J, \) and \( n \) represent the electronic, translational, vibrational, rotational, and nuclear normal modes respectively. Hence, the total internal molecular energy is expressed as the sum of the mode energies:

\[
E = E_e + E_t + E_v + E_J + E_n
\]  

(2-4)
Fig. 2-1 Raman and Rayleigh light scattering processes with respect to the electronic states if the scattering molecule. The energy of the incident photon is depicted as the virtual energy state.
For a typical ensemble of molecules in equilibrium, only the ground electronic state (designated by $X$ as shown in Fig. 2-1) is populated. Thus for normal off-resonance spontaneous Raman scattering, the energy for vibrational-rotational states is expressed as the sum of the vibrational and rotational energy terms:

$$E_{(\nu, J)} = E_\nu + E_J$$  \hspace{1cm} (2-5)$$

where $\nu$ and $J$ are the vibrational and rotational quantum numbers for the vibrational and rotational states of the molecule.

In a diatomic molecule, the vibrational and rotational energy level structures are coupled due to vibration-rotation interaction. These molecular vibrations and rotations alter the moment of inertia by varying the internuclear separation (bond length). Therefore, the anharmonic oscillator and centrifugally stretched rotor must be used to accurately model the energy level structure of a diatomic molecule. The resulting eigenfunctions to Schrödinger’s equation using the anharmonic oscillator and centrifugally-stretched rotor, while neglecting angular momentum coupling, yield the following vibrational and rotational energies:

$$E_\nu = \hbar c [\omega_e (\nu + \frac{1}{2}) - \omega_e x_e (\nu + \frac{1}{2})^2 + \omega_e y_e (\nu + \frac{1}{2})^3 + \omega_e z_e (\nu + \frac{1}{2})^4 + ...]$$  \hspace{1cm} (2-6)$$

$$E_J = \hbar c [BJ(J + 1) - DJ^2(J + 1)^2 + HJ^3(J + 1)^3 + LJ^4(J + 1)^4 + ...]$$  \hspace{1cm} (2-7)$$

where $\omega_e$ is the fundamental vibration frequency, $\omega_e x_e$, $\omega_e y_e$, and $\omega_e z_e$ are anharmonic correction factors, $B$ is the rotational term value, and $D$, $H$, and $L$ are centrifugal stretch correction factors. The rotational and centrifugal stretch correction term values are functions of $\nu$ through vibration-rotation interaction and are given $\nu$ subscripts:

$$B_\nu = B_e - \alpha_e (\nu + \frac{1}{2}) + \rho_e (\nu + \frac{1}{2})^2 - \pi_e (\nu + \frac{1}{2})^3$$  \hspace{1cm} (2-8)$$

$$D_\nu = D_e - \beta_e (\nu + \frac{1}{2}) + \delta_e (\nu + \frac{1}{2})^2$$  \hspace{1cm} (2-9)$$

$$H_\nu = H_e - \gamma_e (\nu + \frac{1}{2})$$  \hspace{1cm} (2-10)$$

$$L_\nu = L_e - \eta_e (\nu + \frac{1}{2})$$  \hspace{1cm} (2-11)$$

where $B_e$, $D_e$, $H_e$, $L_e$, $\alpha_e$, $\rho_e$, $\pi_e$, $\beta_e$, $\delta_e$, $\gamma_e$, and $\eta_e$ are molecular constants. The subscripts $e$ and $\nu$ denote that the quantity is a constant for a given electronic and vibrational level. In theory, the vibrational-rotational interaction can be seen in the expression for $B_\nu$:

$$B_\nu = \frac{\hbar}{8\pi^2 e \mu} \left[ \frac{1}{r_e^2} \right]_\nu$$  \hspace{1cm} (2-12)$$
where $\mu$ is the reduced mass $(m_1m_2/m_1+m_2)$ and $r_e$ is the internuclear distance of the diatomic molecule. Since values of $r_e$ for the numerous vibrational levels of molecule are extremely difficult to compute analytically and are often highly inaccurate, the molecular constants are determined from experimental spectroscopy data using Dunham’s formula (Dunham 1932). Values of the molecular constants for $\text{H}_2$ are listed in Dabrowski (1984).

Homonuclear molecules do not have a permanent dipole moment (polar charge) and therefore radiation is not absorbed or emitted in a single photon interaction when a molecule undergoes a vibrational or rotational transition. Instead, Raman scattering is a two photon process where inelastic scattering of a photon from a molecule in which energy is absorbed from or deposited into a photon as the molecule undergoes a transition into a new vibrational or rotational energy state. This process occurs through the induced dipole moment, $P_{nm}$, which represents the ability of an applied oscillating electric field to induce an electric moment, or change in polarization that alters the potential energy of the molecule. The magnitude of this induced change in polarization/potential energy of the molecule as it undergoes a scattering transition from state $m$ to $n$ is defined as the dot product of the molecule’s polarizability, $\alpha$, which is a Cartesian coordinate $(x,y,z)$ tensor, and the magnitude of the electric field vector of the incident radiation, $E$, or $P_{nm} = \alpha \cdot E$. In simplest terms, the molecular dipole moment, $P_{nm}$, can also be given by $r_e q_N$, the internuclear distance $r_e$ times the charge of the nucleus. It can be clearly seen from this relation that the evaluation of $P_{nm}$ will also provide the scattering probability or scattering cross-section of the molecule since it is a direct function of $r_e$, the larger the internuclear distance the higher the probability of inducing a scattering a transition.

To account for the perturbation of the molecular potential by the electric field, the term $(\alpha_{nm} E)$ must be subtracted (since it is a repulsive potential) from the unperturbed Hamiltonian. After correcting for the perturbation of the potential energy in the Hamiltonian, Schrödinger’s equation can be evaluated to determine the initial and final states, i.e. the allowed transitions of the molecular system. Since the polarizability/induced dipole moment is modulated by the vibrational and rotational motions in the molecule, the selection rules for the allowed Raman transitions are the change in the eigenvalues of the vibrational and rotational eigenfunctions that satisfy the perturbed wave functions, which are determined in the solution of Schrödinger’s equation and by evaluating the expectation value for $\alpha_{nm}$ such that:
where $\Psi_m$ and $\Psi_n$ are the perturbed wave functions for the initial and final states, $r$ is any energy state of the unperturbed molecule, $M_{nr}$ etc. are the transition dipole moment matrix elements associated with states $n$, $m$, and $r$, and $v_{rn}$ and $v_{rm}$ are the energy level differences between states $r$ to $n$ and $r$ to $m$, respectively. The summation of the transition matrix element terms is over all states $r$ and is extremely tedious. Furthermore, the transition dipole matrix elements/scattering cross-sections have not been evaluated to date since the molecular polarizability is a function of the molecular coordinates, time, $E$ and $r_e$, which are functions of the vibrational-rotational interaction and are very difficult to compute with any accuracy.

Fortunately under proper conditions, a simple mathematical expression can be used to approximate $\alpha_{nm}$, thus making the evaluation of Eq. 2-13 and the functional dependence of the scattering intensity with respect to the initial vibrational and rotational states more practical. This simplification in terms of the induced polarizability and polarizability derivatives is known as Placzek’s polarizability theory (Placzek 1934). Placzek’s theory can be used to evaluate Eq. 2-13 providing the following conditions are realized: a) transitions are confined to vibrational and rotational transitions within the ground electronic state; b) the ground electronic state is not degenerate; c) the excitation frequency must be much greater than the vibrational frequency of the molecule, i.e. $\nu_o \gg \nu_{nm}$; and d) the excitation frequency must be much less than the frequency needed for an electronic transition, i.e. $\nu_{rn} \gg \nu_o$ (this is the off resonance condition). Thus, Placzek’s polarizability theory will be briefly described to provide the selection rules for the allowed Raman scattering transitions and for future use in developing the expression for the Raman scattered intensities.

The vibrations/rotations of a homonuclear diatomic molecule perturb the polarizability through fluctuations in the nuclear coordinate. These nuclear fluctuations are very small and since the nuclear coordinates are described in terms of the vibrational/rotational coordinates, the perturbed polarizability can be accurately linearized by a first order Taylor series expansion:

$$\hat{\alpha}(X_i) = \hat{\alpha}_o + \sum_j \left( \frac{\partial \hat{\alpha}}{\partial X_j} \right)_o X_j + ...$$  \hspace{1cm} (2-14)
where the hat denotes a tensor, $\hat{\alpha}_\alpha$ is the $\alpha$ at equilibrium, $X$ is the normal coordinate tensor for the vibrations/rotations associated with vibrational/rotational frequencies $\nu_i$, $\nu_j$, ..., and the summation is over all normal coordinates. Substitution of the Taylor series approximation into the induced dipole moment transition matrix yields:

$$P_{mn} = \langle \psi_n | \hat{\alpha}_\alpha | \psi_m \rangle \cdot E + \langle \psi_n | \frac{\partial \hat{\alpha}}{\partial X} | \psi_m \rangle \cdot E \neq 0$$ (2-15)

Due to orthogonality of the wavefunctions, the first term in Eq. 2-15 describes Rayleigh scattering and is non-zero when for all the molecules sampled the initial and final states, $m$ and $n$ respectively, are identical. In this case the integral reduces to unity and the polarizability/scattering cross-section reduces to the equilibrium value. The second term in Eq. 2-15, which involves the polarizability derivatives, gives the allowed Raman transitions and scattering efficiencies. The derived conditions for Raman scattering are a consequence of the solution to Eq. 2-13 using the harmonic oscillator and rigid rotor wavefunction approximations as previously stated. Thus the allowed vibrational and rotational transitions follow $\Delta \nu = 0, \pm 1$ and $\Delta J = 0, \pm 2$, respectively. Possible combinations of vibrational and rotational transitions allowed by the selection rules have been given a spectroscopic convention. Table 2-1 lists the Rayleigh and Raman scattering combinations and spectroscopic designations.

Eventhough the solution to Eq. 2-15 uses the harmonic oscillator and rigid rotor, the results are still applicable to the anharmonic oscillator and centrifugally stretched rotor. This is true mathematically since the anharmonic oscillator can alter the vibrations or energy of the molecule but it cannot change the symmetry and can therefore be expressed as linear combinations of harmonic oscillator functions, with the same being true of the centrifugally stretched rotor. In addition, an obvious fact of Eq. 2-15 is that Rayleigh scattering is much stronger because it is a first order process compared to Raman scattering which is a function of the polarizability derivatives ($2^{nd}$ order process).

The previous discussion describes how and why a Raman scattered transition occurs when a molecule is perturbed by an oscillating electric field. Using the derived selection rules in conjunction with the quantum nature of light and energy, the difference in frequency/energy of the incident and scattered photon or the change in energy of the molecule can be determined. For the current work only the Stokes Raman branches, designated as $O_v(J)$, $Q_v(J)$, and $S_v(J)$, are of interest. Consequently, the molecular internal energy obeys $\Delta \nu = +1$ and $\Delta J = 0, \pm 2$ and the
Table 2-1. Rayleigh and Raman scattering nomenclature.

<table>
<thead>
<tr>
<th>Transition</th>
<th>Band</th>
<th>Branch</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta \nu = 0, \Delta J = 0$</td>
<td>Rayleigh</td>
<td>-</td>
</tr>
<tr>
<td>$\Delta \nu = 0, \Delta J = +2$</td>
<td>Stokes</td>
<td>Pure Rotational (S)</td>
</tr>
<tr>
<td>$\Delta \nu = 0, \Delta J = -2$</td>
<td>anti-Stokes</td>
<td>Pure Rotational (O)</td>
</tr>
<tr>
<td>$\Delta \nu = +1, \Delta J = +2$</td>
<td>Stokes</td>
<td>S</td>
</tr>
<tr>
<td>$\Delta \nu = +1, \Delta J = 0$</td>
<td>Stokes</td>
<td>Q</td>
</tr>
<tr>
<td>$\Delta \nu = +1, \Delta J = -2$</td>
<td>Stokes</td>
<td>O</td>
</tr>
<tr>
<td>$\Delta \nu = -1, \Delta J = +2$</td>
<td>anti-Stokes</td>
<td>S</td>
</tr>
<tr>
<td>$\Delta \nu = -1, \Delta J = 0$</td>
<td>anti-Stokes</td>
<td>Q</td>
</tr>
<tr>
<td>$\Delta \nu = -1, \Delta J = -2$</td>
<td>anti-Stokes</td>
<td>O</td>
</tr>
</tbody>
</table>
corresponding change in the scattering molecule’s energy from the initial to the final state (Raman shift) of all quantized levels for which transitions are allowed is expressed as:

\[
\frac{\Delta E_{\nu,J}}{hc} = \frac{E' - E''}{hc} = [\omega_e - 2\omega_e x_e (\nu'' + 1) - \alpha_e J(J + 1) - \beta_e J^2 (J + 1)^2 + ...]
\]  

(2-16)

where \( E' \) is the energy of the final state, \( E'' \) is the energy of the initial state, and \( \nu'' \) is \( \nu \) for the initial energy state. Energy lost by the interacting photons to the scattering molecule is given by Eq. 2-16, and substitution into Eq. 2-1 provides the frequencies of the Stokes Raman scattered light, \( \nu_S \), which depends upon \( \nu'', J \), and the incident photon’s frequency, \( \nu_0 \), through:

\[
\nu_S = (\nu_0 - \frac{\Delta E_{\nu,J}}{hc}) = [\nu_0 - [\omega_e - 2\omega_e x_e (\nu'' + 1) - \alpha_e J(J + 1) - \beta_e J^2 (J + 1)^2 + ...]]
\]  

(2-17)

From Eq. 2-17, it is apparent that the fundamental vibrational frequency, \( \omega_e \), approximately determines \( \nu_S \). The anharmonic correction terms, \( \omega_e x_e \),... group together Raman transitions according to \( \nu'' \). This slight difference in frequency shift for each initial vibrational level is what allows the vibrational population distribution to be determined. Finally, within each vibrational state the \( J \) value determines a transition’s exact \( \nu_S \). Due to the hierarchy of the energy storage modes and since the vibrational energy levels are much more widely spaced than the rotational energy levels, each vibrational state has a unique rotational distribution. As will be shown through further discussion, these spectroscopically distinctive features form the basis of using Raman scattering for thermometry.

Additionally, \( \nu_S \) also depends upon temperature, \( T \), and density, \( \rho \), through vibrational perturbations, which can either reduce or increase \( \Delta E_{\nu,J} \) through short-range repulsive and long-range attractive forces (May et al. 1964). A correction term for \( \Delta E_{\nu,J}/hc \) can be added to Eq. 2-17 for the \( \rho \), \( T \), \( J \), and collision partner-dependent shift of \( \nu_S \). Values of corrections for \( \Delta E_{\nu,J}/hc \) are available for \( \text{H}_2 \) in \( \text{H}_2 \) (May et al. 1964, Lallemand and Simova 1968, and Hussong 2002), \( \text{H}_2 \) in \( \text{N}_2 \) (Lallemand and Simova 1968, Sinclair et al. 1996, and Hussong 2002), \( \text{H}_2 \) in \( \text{H}_2\text{O} \) (Hussong 2002), and \( \text{H}_2 \) in \( \text{Ar}, \text{He}, \text{or CH}_4 \) (Sinclair et al. 1996). These collision partner-dependent corrections for species \( j \) diffusing into species \( i \), \( \delta_{i,j} \), are determined from experimental data for each Raman transition and are of the form:

\[
\delta_{i,j} = \delta_i^{+} + \tilde{\delta}^{+} \cdot \sqrt{T}
\]  

(2-18)

For the \( \text{H}_2\text{-N}_2 \) mixtures and rich \( \text{H}_2\)-air flames examined in this work, the important collision partners for \( \text{H}_2 \) are \( \text{H}_2, \text{N}_2, \text{and H}_2\text{O} \). Values for the components of \( \delta_{i,j} \) are listed in Table 2-2.
Table 2-2. Collisional lineshift parameter values for H$_2$-H$_2$, N$_2$, H$_2$O collision partners (data taken from Sinclair et al. 1996 and Hussong 2002).

<table>
<thead>
<tr>
<th>$J$</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>&gt;=7</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta_{o}^{H_2-H_2}$</td>
<td>-14.44</td>
<td>-17.04</td>
<td>-15.07</td>
<td>-14.73</td>
<td>-14.96</td>
<td>-14.87</td>
<td>-14.87</td>
<td>-14.87</td>
</tr>
<tr>
<td>$\delta^{H_2-H_2}$</td>
<td>0.7074</td>
<td>0.8044</td>
<td>0.7615</td>
<td>0.7414</td>
<td>0.7775</td>
<td>0.7797</td>
<td>0.78</td>
<td>0.78</td>
</tr>
<tr>
<td>$\delta_{o}^{H_2-N_2}$</td>
<td>-23.2</td>
<td>-27.2</td>
<td>-27.4</td>
<td>-27.4</td>
<td>-28.9</td>
<td>-29.8</td>
<td>-29.9</td>
<td>-29.9</td>
</tr>
<tr>
<td>$\delta^{H_2-N_2}$</td>
<td>0.8</td>
<td>1.08</td>
<td>1.12</td>
<td>1.14</td>
<td>1.23</td>
<td>1.27</td>
<td>1.27</td>
<td>1.3</td>
</tr>
<tr>
<td>$\delta_{o}^{H_2-H_2O}$</td>
<td>-65.0</td>
<td>-52.4</td>
<td>-30.1</td>
<td>28.95</td>
<td>32.0</td>
<td>39.1</td>
<td>39.1</td>
<td>39.1</td>
</tr>
<tr>
<td>$\delta^{H_2-H_2O}$</td>
<td>1.08</td>
<td>0.79</td>
<td>0.357</td>
<td>0.347</td>
<td>0.49</td>
<td>0.75</td>
<td>0.75</td>
<td>0.75</td>
</tr>
</tbody>
</table>

$\delta_{o}$ is expressed in 10$^{-3}$cm$^{-1}$/amagat

$\delta$ is expressed in 10$^{-3}$cm$^{-1}$/amagat/K$^{1/2}$.

Collision data for H$_2$-O$_2$ collision partners is currently unavailable and is therefore modeled using H$_2$-N$_2$ collision data, since the molecular mass of O$_2$ (32 g/mol) is similar to N$_2$ (28 g/mol).
For multi-component mixtures, the total H$_2$ collisional energy shift is determined using Wilke’s theorem:

$$\delta_{H_2,\text{tot}} = \sum_j \rho \cdot C_j \cdot \delta_{H_2-j}$$

where \(\rho\) is the gas density in amagat units determined from Redlich-Kwong data (Redlich-Kwong 1949), \(C_j\) is the colliding species concentration based on the composition of the equilibrium gas mixture, and the summation is over all relevant collision partner pairs.

For an ensemble of freely orientable scattering molecules undergoing a transition from state \(m\) to \(n\), the Raman scattering intensity is related to the incident radiation, transition energy, and the induced dipole moment/transition probability matrix through,

$$I_{nm} \propto (v_v \pm v_{nm})^4 \cdot P_{nm}^2 \cdot N_n,$$

where \(N_n\) is the population of the initial level. Assuming thermodynamic equilibrium and a Boltzmann distribution of the population of states for an ensemble of molecules in conjunction with Placzek’s polarizability theory, the intensity of a Stokes Raman transition, \(I_{(v,J)}\), is related to \(v''\), \(J\), and \(T\) by:

$$I_{(v,J)} \propto v''^4 \cdot \frac{(v'' + 1)P_J}{v_v} \cdot g_J (2J + 1) \cdot \exp\left(-\frac{E''_{(v,J)}}{kT}\right)$$

where \((v'' + 1)P_J/v_v\) is the transition probability (scattering cross-section) that results from evaluation of \(P_{nm}^2\), \(v_v\) is the frequency of the vibrational state, and \(Q\) is the \(T\)-dependent partition function expressed as the product of the mode partition functions:

$$Q = Q_{\text{rot-nc}} \cdot Q_{\text{vib}} = \sum_J g_J (2J + 1) e^{-E_J/kT} \sum_v e^{-E_v/kT}$$

Boltzmann’s constant is given as \(k\), \(g_J\) is the relative degeneracy for rotation-nuclear spin coupling, and \(E_J\) and \(E_v\) are the rotational and vibrational energies respectively. Thus, the intensity of a Raman transition is a direct function of the population fraction of the particular vibrational-rotational state, which provides the needed \(T\) dependence, scaled by the corresponding transition probability.

The determination of the rotational-nuclear spin degeneracy is a complex argument that involves the symmetry of the wavefunctions and spin of the nuclei of the atoms. From quantum theory, i.e. the Pauli exclusion principle, it is shown that particles with integral nuclear spin (Bosons or nuclei of even mass number) have symmetric states total system wavefunctions, while particles of half integral nuclear spin (Fermions or nuclei of odd mass number) have anti-
symmetric total system wavefunctions. Using this precept, the proceeding discussion will develop the expressions for the rotational-nuclear spin degeneracy for homonuclear diatomic molecules (e.g. H₂, O₂, N₂ ...) through an analysis of Eq. 2-3.

The electronic wavefunction, \( \Psi_e \), is always assumed symmetric in the ground state, the translational wavefunction, \( \Psi_t \), is only a function of the position of the molecule’s nuclei, and the vibrational wavefunction, \( \Psi_v \), depends only on the internuclear separation distance; therefore, the total system wavefunction (Eq. 2-3), in regards to symmetry, reduces to \( \Psi = \Psi_j \Psi_n \). As a result, \( \Psi_j \Psi_n \) for a molecule with identical nuclei of odd mass number is anti-symmetric and \( \Psi_j \Psi_n \) for a molecule with identical nuclei of even mass number is symmetric. Examination of \( \Psi_n \) reveals that the ground level of each nucleus is degenerate due to nuclear spin (each H nucleus has 2 possible spin states, spin up or spin down) and can be expressed as \( g_n = 2m_n + 1 \), where \( m_n \) is the nuclear spin quantum number. Since each nucleus has \( g_n \) total wavefunctions, statistics dictates that the total nuclear degeneracy is a combination of the symmetric and anti-symmetric nuclear wavefunctions according to:

\[
\begin{align*}
g_n^2 &= \frac{g_n (g_n + 1)}{2} + \frac{g_n (g_n - 1)}{2} \\
&= (2-22)
\end{align*}
\]

For Bosons, or molecules with even mass number and nuclei of integral spin, the first term in Eq. 2-22 is the contribution due to symmetric nuclear spin states where as the second term is due to the anti-symmetric nuclear spin states, and vice versa for Fermions, or molecules with odd mass number and nuclei of half integral spin.

The remaining problem in solving the rotational-nuclear spin degeneracy involves the symmetry of the rotational wavefunctions. The symmetry of the rotational wavefunction, as determined from examination of the Legendre functions used to approximate the rotational states, is determined from \((-1)^J\) raised to the \(J\)th power. When \((-1)^J\) is positive the rotational wavefunction is symmetric and can only represent even \( J \) states and when \((-1)^J\) is negative the rotational wavefunction is anti-symmetric and can only represent odd \( J \) states. Since the total wavefunction is the product of \( \Psi_j \Psi_n \) and nuclear spin symmetry can be either symmetric or anti-symmetric, the overall rotational-nuclear spin must be evaluated in terms of the rotational states \( (J) \) to meet the symmetry requirements of the molecule’s total wavefunction. For example consider a homonuclear molecule with nuclei of odd mass number, the total wavefunction is anti-symmetric and therefore only symmetric nuclear spin states are accessible for odd \( J \) states.
while only anti-symmetric nuclear spin states are accessible for even $J$ states. The total rotational-nuclear spin degeneracy, applying rotational symmetry arguments to Eq. 2-22, for Fermions becomes:

$$g_J = \left( \frac{g_n(g_n - 1)}{2} \right)_{J=0,2,4,6,...} \text{ or } \left( \frac{g_n(g_n + 1)}{2} \right)_{J=1,3,5,7,...}$$  \hspace{1cm} (2-23)

Conversely, a homonuclear molecule with nuclei of even mass number has a symmetric total wavefunction and therefore only anti-symmetric nuclear spin states are accessible for odd $J$ states while only symmetric nuclear spin states are accessible for even $J$ states. Thus for Bosons, the rotational-nuclear spin degeneracy is:

$$g_J = \left( \frac{g_n(g_n + 1)}{2} \right)_{J=0,2,4,6,...} \text{ or } \left( \frac{g_n(g_n - 1)}{2} \right)_{J=1,3,5,7,...}$$  \hspace{1cm} (2-24)

To illustrate the impact of rotational-nuclear spin statistics, $g_J$ for O$_2$, N$_2$, and H$_2$ will be determined. Both O$_2$ and N$_2$ are bosons, or have nuclei of even mass number, and thus $g_J$ is determined using Eq. 2-24. The nuclei of the O atoms have a nuclear spin of $m_n = 0$ (i.e. no spin) and consequently a degeneracy of $g_n = 1$. This results in a value of $g_J = 1$ for even $J$ states and $g_J = 0$ for odd $J$ states, or none of the odd $J$ states are populated resulting in the absence of the odd rotational transitions in the Raman spectrum of O$_2$. For N$_2$, the spin quantum number $m_n = 1$ and $g_n = 3$ to yield $g_J = 6$ for even $J$ states and $g_J = 3$ for odd $J$ states, or the even $J$ states are 2x more populated than the odd $J$ states, thus producing an alternating even/odd intensity pattern of 2:1. In contrast to O$_2$ and N$_2$, H$_2$ is a fermion with $m_n = 1/2$ and $g_n = 2$, thus from Eq. 2-23 $g_J = 1$ for even $J$ states and $g_J = 3$ for odd $J$ states. Since there are 3 symmetric nuclear spin states that can only combine with odd $J$ states and 1 anti-symmetric nuclear spin state that can only combine with even $J$ states, there will be 3x as many transitions between odd $J$ states as there are transitions between even $J$ states or the Raman spectrum of H$_2$ will have an alternating intensity pattern of 3:1. The rotational-nuclear spin degeneracy is constant for all rotational levels of heteronuclear diatomic molecules, i.e. the Raman spectrum exhibits 1:1 even/odd $J$ transition intensities. These $g_J$ statistical variations on the intensity pattern of Raman transitions have been verified by experimental spectra.

For certain molecules, namely H$_2$ which is the species of interest for this work, the expressions for $g_J$ in Eq.’s 2-23 and 2-24 are not completely accurate at low temperatures. This artifact is due to nuclear spin symmetry and the rather large characteristic rotational temperature,
$T_r$, 85.4K for H$_2$, which is the temperature at which the rotational modes are fully activated. The first term in Eq. 2-23 represents the contribution of molecules in symmetric $J$ states and anti-symmetric nuclear states (paired spins), such molecules are called para-H$_2$. The second term represents the contribution of molecules in anti-symmetric $J$ states and symmetric nuclear states (parallel spin), and these are termed ortho-H$_2$. It is apparent from Eq. 2-21 that the two contribute differently to $Q_{ro-nuc}$, thus any sample of H$_2$ will consist of a mixture of the two molecular forms. Normal H$_2$ at room temperatures (high $T$ limit) exists in an equilibrium ortho/para ratio of 3:1, or 75%/25%. As $T$ decreases, the nuclear spins will “flip” to change the ratio in favor of the para form of H$_2$ to accommodate for the equilibrium distribution of molecules among the $J$ states which favor the even $J$ states. Thus from the definition of $Q_{ro-nuc}$, the equilibrium ratio of ortho/para H$_2$ is $T$ dependent and is given by comparing $Q_{ro-nuc}$ for the odd and even $J$ states:

$$
\frac{N_{ortho}}{N_{para}} = \frac{3 \sum_{J=1,3,5...} (2J + 1) \exp \left[ -\frac{T_r}{T} J(J + 1) \right]}{1 \sum_{J=0,2,4...} (2J + 1) \exp \left[ -\frac{T_r}{T} J(J + 1) \right]} 
$$

(2-25)

At low temperatures mixtures of ortho and para-H$_2$ self convert to para-H$_2$ by collisions; the spin angular momentum of the ortho-H$_2$ molecules creates a magnetic interaction that induces spin “flip”. However, this self conversion rate is extremely slow and requires hundreds of hours to obtain the equilibrium concentration of para-H$_2$. This explains why H$_2$ cooled from room temperature exhibits properties in closer agreement with normal H$_2$ (75%/25% ortho/para). The ortho-to-para conversion rate can be increased if the sample of H$_2$ is cooled in the presence of a metal catalyst; the H$_2$ adheres to the surface of the metal and dissociates to H-atoms which then recombine under equilibrium conditions (correct spin pairs) and the properties agree with equilibrium predictions. Similarly to the cooling of room temperature H$_2$, if cooled equilibrium H$_2$ is rapidly heated, as in combustion using LH$_2$, the thermodynamic properties are in closer agreement with those of the initial cooled equilibrium H$_2$ due the long equilibrium conversion time.

The $((\nu'' + 1)P_J)/\nu_v$ transition probability/scattering cross-section term in Eq. 2-20 is a consequence of polarizability theory. The $(\nu'' + 1)/\nu_v$ factor is the intensity scaling law for vibrational transitions that accounts for the increase in polarization of a molecule with increasing
ν″. From theory, this intensity scaling factor is a direct result of the matrix element integration of Eq. 2-15. Physically, the bond length of the molecule, or internuclear separation, is stretched as ν″ increases, thus increasing the ability of an incident electric field to induce a change in polarization in a vibrationally excited molecule compared to a molecule in the ground vibrational state. The $P_J$ term is the $J$-dependent Placzek-Teller coefficient, which is a function of the polarizability components (the molecular isotropy and anisotropy) that depend on the frequency and polarization of the incident radiation and the geometry of the scattering system. Vibrational perturbations/transitions in the molecule are isotropic in nature and hence the normal coordinate polarizability components (xx, yy, zz or diagonal components of the polarizability tensor) define the isotropic polarizability $\alpha$. In addition to the isotropic perturbations, rotational transitions also occur if the incident electric field can induce an off-axis polarization or anisotropic polarization $\gamma$ (all the components of the polarizability tensor). These functions can be determined for various scattering configurations by using Placzek’s polarizability theory and the polarization/scattering geometry tables in Long (1977) to evaluate $P_{nm}^2$. For example, Table 2-3 lists the $P_J$ values for the Rayleigh and Raman scattering processes for a completely linearly polarized incident radiation source with observation/collection at 90° to the direction of propagation (Fig. 2-2).

The previous theoretical discussion on Raman scattering is based on the assumption that $\nu_r >> \nu_o$ for all electronically excited states $\nu_r$. This is not completely valid if the frequency of the incident light source approaches an allowed electronic transition. As $\nu_o$ approaches $\nu_r$, the Raman scattering activity increases above the normal $(\nu_o+\nu_{nm})^4$ scaling law because the denominator in the summation of Eq. 2-13 decreases. During this near-resonance enhancement condition, the use of Placzek’s polarizability theory is not completely valid and the Raman scattering intensity must be predicted by calculating all the $M_{nr}$ and $M_{rm}$ in Eq. 2-13. However, this calculation can be facilitated by single resonance theory (Albrecht and Hutley 1971, Bischel and Black 1983, Wehrmeyer et al. 1992a and 1992b, and Cheng et al. 2002), which approximates all the excited electronic states with a single “effective” intermediate state $i$. Based on this theory to describe the polarizability dependence on the incident radiation frequency for near-resonance conditions, the intensity for a Raman transition becomes the product of Eq. 2-20 and the term
Table 2-3. Example showing the evaluation of $P_J$ using a linearly polarized incident radiation source with observation/collection at 90° to the direction of propagation (using scattering geometry configurations and tables in Long 1977).

<table>
<thead>
<tr>
<th>Band</th>
<th>Branch</th>
<th>Selection Rules</th>
<th>$P_J$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rayleigh</td>
<td>-</td>
<td>$\Delta \nu=0$, $\Delta J=0$</td>
<td>$\alpha_0^2 + \frac{7}{45} b_{J,J} \gamma_0^2$</td>
</tr>
<tr>
<td>Pure Rotational Raman</td>
<td>$O$ and $S$</td>
<td>$\Delta \nu=0$, $\Delta J=\pm 2$</td>
<td>$\frac{7}{45} b_{J+2,J} \gamma_0^2$</td>
</tr>
<tr>
<td>Vibrational Raman</td>
<td>$Q$</td>
<td>$\Delta \nu=+1$, $\Delta J=0$</td>
<td>$\alpha_r^2 + \frac{7}{45} b_{J,J} \gamma_r^2$</td>
</tr>
<tr>
<td>Vibrational Raman</td>
<td>$O$ and $S$</td>
<td>$\Delta \nu=+1$, $\Delta J=\pm 2$</td>
<td>$\frac{7}{45} b_{J+2,J} \gamma_r^2$</td>
</tr>
</tbody>
</table>

$\alpha_0$ and $\gamma_0$ are the equilibrium isotropic and anisotropic polarizability, respectively. $\alpha_r$ and $\gamma_r$ are the derived isotropic and anisotropic polarizability, respectively.

\[
b_{J,J} = \frac{J(J+1)}{(2J-1)(2J+3)} \quad b_{J+2,J} = \frac{3(J+1)(J+2)}{2(2J+1)(2J+3)} \quad b_{J-2,J} = \frac{3J(J-1)}{2(2J+1)(2J-1)}
\]

Fig. 2-2 Typical experimental Raman scattering system configuration.
where \( v_{i,n} \) is the molecule specific intermediate state frequency and the subtraction of \( v_{nm} \) from \( v_{i,n} \) accounts for the initial energy level dependence. The single resonance intermediate state frequencies determined by Bischel and Black (1983) are listed in Table 2-4 along with the energy difference between the ground and first excited electronic states.

This extra near-resonant enhancement is depicted in Fig. 2-3 by showing that vibrationally excited states and their virtual Raman energy levels lie closer to the intermediate state as the frequency of the incident radiation increases (Wehrmeyer, 1990). For example, a KrF laser with a UV frequency of 40257.487\,\text{cm}^{-1}, which is used for this research, has a near-resonant enhancement for the vibrational H\(_2\) Stokes Raman scattering \( \nu = 1 \rightarrow 2 \) transition of \(~0.5\%\) greater than the resonant enhancement for the \( \nu = 0 \rightarrow 1 \) transition. The calculated resonant enhancement for H\(_2\) is not as significant as for other diatomic molecules, such as O\(_2\) where \( \nu = 1 \rightarrow 2 \) is 26\% greater than \( \nu = 0 \rightarrow 1 \), because of its large energy gap between the ground and first excited electronic energy levels \((A \leftarrow X)\), but the minor enhancement can still introduce error in the temperature measurement if Eq. 2-26 is not included in Eq. 2-20 (Wehrmeyer 1992b and Shirley 1990).

The positions and intensities of spectral lines, using the equations in the previous discussion, are often shown in a “stick” diagram, where discrete lines are substituted for each spectral feature. Stick diagrams for the H\(_2\) Stokes vibrational Q-branch Raman spectrum are shown in Fig. 2-4(a-c) for two temperatures, 700K (Figs. 2-4a-b) and 3400K (Fig. 2-4c). Here the lines are labeled by the notation \( X_{\nu}(J^\gamma) \) where \( X = O, Q, S \) for the allowed \( \Delta J = -2, 0, 2 \) respectively. The 3:1 ratio of the even and odd \( J \) populations caused by nuclear spin statistics for a heated mixture of normal H\(_2\) is clearly evident in Fig. 2-4a. To represent the Raman spectra from combustion of LH\(_2\) in the rocket-engine like test article of the work, Fig. 2-4b depicts the 1:1 ratio of the even and odd \( J \) states for an initial cooled equilibrium mixture of H\(_2\) that has been rapidly heated. At low temperatures, as shown at 700K in Figs 2-4a and 2-4b, only the first few rotational levels for the ground vibrational state are significantly populated, and as temperature increases, shown at 3400K in Fig. 2-4c, more rotational levels in the ground and excited vibrational states become populated due to the \( T \) dependence of the Boltzmann distribution.
<table>
<thead>
<tr>
<th>Molecular Species</th>
<th>Intermediate State Frequencies (Bischel and Black 1983)</th>
<th>Electronic Energy Level Spacing (Huber and Herzberg 1979)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂</td>
<td>56,900 cm⁻¹</td>
<td>$B^3Σ_u^- \leftarrow X^3Σ_g^- \ 49,793 \text{cm}^{-1}$</td>
</tr>
<tr>
<td>N₂</td>
<td>89,500 cm⁻¹</td>
<td>$a^1π_g \leftarrow X^1Σ_g^+ \ 69,283 \text{cm}^{-1}$</td>
</tr>
<tr>
<td>H₂</td>
<td>84,800 cm⁻¹</td>
<td>$B^1Σ_u^+ \leftarrow X^1Σ_g^+ \ 91,700 \text{cm}^{-1}$</td>
</tr>
</tbody>
</table>
Fig. 2-3  Near resonant enhancement showing proximity of excited vibrational levels with the intermediate state.
Figs. 2-4 “Stick” diagrams of the H₂ Stokes vibrational $Q$-branch Raman bandshape: a) normal H₂ heated to 700 K; b) cooled equilibrium H₂ at 77K heated to 700K; and c) normal H₂ heated to 3400K.
function in Eq. 2-20. This $T$ dependent change in the spectral bandshape is the basis for the contour-fit temperature measurement technique.

### 2.2 Spectral Linewidths and Lineshapes

The experimentally observed spectral lines that result from transitions between energy levels in molecules are not monochromatic, i.e. infinitely narrow as in the stick diagram, because of the Heisenberg Uncertainty Principle and radiation damping that is inherent in any radiating system that loses energy. Since the energy of a transition cannot be precisely defined and radiation damping leads to broadening of the spectral lines, the spectral profile of the transition shows a distribution of energies/frequencies. This small spread in energy is termed the natural linewidth and the distribution of the intensity, $I(\nu)$, in the spectrum for a transition centered at frequency $\nu$, is described by the dispersion formula (Sobel’man 1972):

$$I(\nu) = \int_{-\infty}^{\infty} I_o \frac{\gamma}{2\pi} \frac{d\nu}{(\nu - \nu_r)^2 + \gamma^2/4}$$  \hspace{1cm} (2-27)

where $I_o$ is the peak center intensity and $\gamma$ is the radiation damping constant (cm$^{-1}$) and for a linear harmonic oscillator is given by:

$$\gamma = \frac{1}{2\pi\varepsilon_0} \cdot \frac{2e^2}{3m_e c^2} \nu_r$$  \hspace{1cm} (2-28)

where $m_e$ and $e$ are the electron mass and charge, respectively. The term $\varepsilon_0$ is the permittivity of free space, $\varepsilon_0 = 8.854\times10^{-12}$ e$^2$/N-m$^2$. The radiation damping constant, $\gamma$, is also referred to as the natural radiation width of a line because it is the full width at half maximum from Eq. 2-16. It also describes the rate of energy loss by radiation $E = E_0 e^{-\gamma t}$. Assuming infinite instrumental resolution and no external damping effects, spectral lines with intensity profiles described by Eq. 2-27 are only observed for incident radiation frequency bandwidths $\Delta \nu_0 << \gamma$; for 40258 cm$^{-1}$ excitation with $\Delta \nu_0 = 0.8$ cm$^{-1}$ (0.005 nm) $\gamma = 3\times10^{-6}$ cm$^{-1}$, thus indicating that most narrow bandwidth laser sources broaden spectral lines.

The width of spectral lines, $\Gamma$ (in cm$^{-1}$), is greater than the natural radiation width and $I(\nu)$ is not accurately described by Eq. 2-27. Additionally, the spectral linewidth and intensity distribution is a function of $T$, $\rho$, molecular velocities, collisions and collision partners, and
collection geometry. In accordance with the Doppler principle, the frequency of a scattered photon from a molecule with thermal motion of velocity, \( v \), either toward or away from the direction of observation results in shifts to higher or lower frequencies, respectively. The Doppler linewidth function, \( \Gamma_{Dopp} \), is obtained by determining the Doppler shift for the scattered photon from each molecule and then averaging over the velocity distribution of all the scattered photons from the ensemble of molecules. The distribution of the scattered photon velocities from the radiating molecules is given by Maxwellian statistics. At low \( \rho \), where collisions are rare and the Doppler shift is equal to the thermal velocity of the molecule, the spectral lines have a Doppler-broadened Gaussian lineshape with a linewidth, \( \Gamma_{Dopp} \) (\( \text{cm}^{-1} \)), that depends upon \( T \), \( \nu_L \), \( E' \rightarrow E'' \), and the angle, \( \theta \), between incident and scattered photon directions (Weber 1973):

\[
\Gamma_{Dopp} = \frac{2}{c} \left[ 2 \ln(2) \frac{kT}{m} \right]^{\frac{1}{2}} \times \left[ 4 \left( \nu_o^2 + \nu_o \frac{E' - E''}{hc} \right) \sin^2 \frac{\theta}{2} + \left( \frac{E' - E''}{hc} \right)^2 \right]^{\frac{1}{2}} \quad (2-29)
\]

where \( m \) is the molecular mass. Thus \( \Gamma_{Dopp} \) is a minimum for forward scattering (\( \theta = 0^\circ \)) and a maximum for backward scattering (\( \theta = 180^\circ \)) and intermediate for \( \theta = 90^\circ \). The corresponding Doppler-broadened Gaussian lineshape is given by:

\[
I_{(\nu)} = \int_{-\infty}^{\infty} I_o e^{-4 \ln(2)(\nu - \nu_o)/\Gamma_{Dopp}^2} d\nu \quad (2-30)
\]

As \( \rho \) increases, Doppler broadening of spectral lines decreases because of changes in the molecule’s velocity due to the increasing number of collisions. From the uncertainty principle, a Doppler shifted photon can only give velocity information for displacements of a molecule greater than \( 1/(2\pi \nu_S) \); therefore, the measured Doppler shift of the scattered photon is the mean velocity averaged across this distance (Murray and Javan 1972). For an increasing number of velocity changing collisions experienced through this travel length, the scattering molecule’s average velocity and Doppler shift will approach zero. The reduced mean velocity of the molecule yields spectral lines with a narrower lineshape than the usual Doppler profile. This collisional narrowing, or more often referred to as Dicke line narrowing, can be thought of as a viscous drag exerted on the scattered photon that increases with increasing \( \rho \). If the mean free path \( < 1/(2\pi \nu_S) \), the spectral lines have a Dicke-narrowed Lorenztian lineshape with linewidths, \( \Gamma_{Dicke} \) (\( \text{cm}^{-1} \)) given by:
\[
\Gamma_{\text{Dicke}} = \left[ \frac{4\pi D_o}{c\rho} \right] \times \left[ 4 \left( v_o^2 + v_o \frac{E'' - E'}{hc} \sin^2 \frac{\theta}{2} + \left( \frac{E'' - E'}{hc} \right)^2 \right) \right]
\]

(2-31)

where \( D_o \), in \((\text{cm}^2 \text{ amagat})/\text{sec}\), is an “optical” diffusion coefficient \( \approx 1.13 \times \) molecular diffusion coefficient at 1000K (Rahn et al. 1991 and Bergmann and Stricker 1995). One amagat = \( \rho \) at 1atm, 273K. The Dicke narrowed linewidth is similar to the Doppler linewidth except that the thermal motion term in Eq. 2-29 is replaced by the inverse of the collision rate in Eq. 2-31. The Dicke-narrowed Lorentzian lineshape function is given by:

\[
I_o = \int_{-\infty}^{\infty} I_o \frac{(\Gamma_{\text{Dicke}}/2)^2}{(v - \nu)^2 + (\Gamma_{\text{Dicke}}/2)^2} d\nu
\]

(2-32)

For even larger \( \rho \), the increased frequency of collisions terminate the scattering process. A finite-lived wavetrain results from the collisions with a frequency spread inversely proportional to its duration. These collisions interrupt the interaction of the molecule with the incident radiation and lead to further line broadening. The lineshape is determined from the average response of the ensemble of molecules, which is a function of the distribution of collision times. The collisionally-broadened lines can be modeled with Lorentzian lineshape functions (Eq. 2-32) of linewidth, \( \Gamma_{\text{Coll.Broad}} \), given by:

\[
\Gamma_{\text{Coll.Broad}} = 2\gamma^{o}_{j,j-total}\rho
\]

(2-33)

where \( \gamma^{o}_{j,j-total} \) is the pressure induced collisional broadening coefficient \((\text{cm}^{-1}/\text{amagat})\), calculated in a similar manner to Eq. 2-19 for multi-component mixtures, dependent on \( J, \rho, \) collision partner, and \( T \):

\[
\gamma^{o}_{j,j-total} = \sum_k C_k \gamma^{o}_{j,j-k} \quad \text{and} \quad \gamma^{o}_{j,j-k} = \gamma^{i-k}_o + \tilde{\gamma}^{i-k} \cdot T
\]

(2-34)

The index \( J \) represents individual rotational states, \( i \) is the Raman species of interest, and the summation is over all colliding species \( k \). Values of \( \gamma^{o}_{j,j-k} \), listed in Table 2-5, have been determined experimentally for H\(_2\)-H\(_2\), H\(_2\)-N\(_2\), and H\(_2\)-H\(_2\)O (Hussong et al. 2000) and H\(_2\)-H\(_2\)O (Clauss et al. 2002).

Figure 2-5, using the aforementioned lineshape functions, shows the theoretical profiles for the \( Q_0(0) \) and \( Q_0(I) \) transitions of H\(_2\) as a function of \( \rho \) at 300 K for a dilute mixture of H\(_2\) in N\(_2\). The shift in frequency of the Raman lines with increasing density is a direct result of the \( \rho-, T-, J-, \) and collision partner-dependent \( \Delta E_{(v,j)}/hc \) correction term included in Eq. 2-17 and
Table 2-5. Collisional linebroadening parameter values for H$_2$-H$_2$, N$_2$, H$_2$O collision partners (data taken from Hussong 2002 and Clauss et al. 2002).

<table>
<thead>
<tr>
<th>J</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>&gt;=7</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma_{o}^{H_2-H_2}$</td>
<td>-1.38</td>
<td>-0.61</td>
<td>-0.2</td>
<td>0.98</td>
<td>0.39</td>
<td>-0.18</td>
<td>-0.18</td>
<td>-0.18</td>
</tr>
<tr>
<td>$\gamma_{i}^{H_2-H_2}$</td>
<td>9.08</td>
<td>5.0</td>
<td>5.48</td>
<td>3.96</td>
<td>4.25</td>
<td>4.38</td>
<td>4.38</td>
<td>4.38</td>
</tr>
<tr>
<td>$\gamma_{o}^{H_2-N_2}$</td>
<td>-1.1</td>
<td>0.2</td>
<td>-0.3</td>
<td>-0.1</td>
<td>-0.4</td>
<td>-0.6</td>
<td>-1</td>
<td>-3</td>
</tr>
<tr>
<td>$\gamma_{i}^{H_2-N_2}$</td>
<td>13.9</td>
<td>6.2</td>
<td>8.6</td>
<td>7.9</td>
<td>6.6</td>
<td>6.5</td>
<td>8</td>
<td>9</td>
</tr>
<tr>
<td>$\gamma_{o}^{H_2-H_2O}$</td>
<td>-14.84</td>
<td>71</td>
<td>6.2</td>
<td>47</td>
<td>17.7</td>
<td>41.7</td>
<td>41.7</td>
<td>41.7</td>
</tr>
<tr>
<td>$\gamma_{i}^{H_2-H_2O}$</td>
<td>97.7</td>
<td>131</td>
<td>28.6</td>
<td>88</td>
<td>43.4</td>
<td>62.3</td>
<td>62.3</td>
<td>62.3</td>
</tr>
<tr>
<td>$\gamma_{i}^{H_2-H_2O}$</td>
<td>0.0</td>
<td>-5.6</td>
<td>0.0</td>
<td>-3.5</td>
<td>-1.45</td>
<td>-2.95</td>
<td>-2.95</td>
<td>-2.95</td>
</tr>
</tbody>
</table>

For H$_2$O, $\gamma_{j}^{o} = \gamma_{o}^{i-j} + \gamma_{i-j}^{o} \cdot T + \gamma_{i-j}^{o} \sqrt{T}$

$\gamma_o$ is expressed in $10^{-3}$ cm$^{-1}$/amagat

$\gamma_i$ is expressed in $10^{-6}$ cm$^{-1}$/amagat/K$^{1/2}$.

$\gamma_{i}^{o}$ is expressed in $10^{-3}$ cm$^{-1}$/amagat/K$^{1/2}$.

Collision data for H$_2$-O$_2$ collision partners is currently unavailable and is therefore modeled using H$_2$-N$_2$ collision data, since the molecular mass of O$_2$ (32 g/mol) is similar to N$_2$ (28 g/gmol).
Fig. 2-5  Theoretical calculation of the first two rotational lines of the H₂ Stokes vibrational $Q$-branch spectrum at 300 K including natural linewidths for three pressures. Assumes dilute H₂ in N₂.
discussed on page 25. At 1 atm (0.911 amagat), the spectral lines are slightly Doppler broadened; however, as illustrated by the smaller $\Gamma$ at 10 atm (9.14 amagat), collisional/Dicke-narrowing occurs and even further increases in $\rho$ results in pressure broadening, as shown by the larger $\Gamma$ at 100 atm (91.9 amagat), due to the increasing frequency of molecular collisions. Most importantly, the rotational lines are fully resolved despite significant broadening at high $\rho$, remaining so at pressures exceeding 370 atm (not shown), which is a pressure expected in advanced rocket engines.

As described by theory and illustrated in Fig. 2-5, a spectral line’s width and intensity distribution is inherently a strong function of $\rho$. Thus, $\Gamma$ for a spectral line is determined from a combination of Eqs. 2-29, 2-31, and 2-33 over the appropriate $\rho$ ranges: $\Gamma = \Gamma_{\text{Dopp}}$ at low $\rho$, $\Gamma = \Gamma_{\text{Dicke}}$ at medium $\rho$, and $\Gamma = \Gamma_{\text{Coll. Broad}}$ at high $\rho$. The corresponding natural lineshape for a Raman transition can be simply approximated by either a Gaussian function at low $\rho$ for Doppler broadened lines or a Lorentzian function at medium to high $\rho$ for Dicke narrowed and collisionally broadened lines, although Voigt or Galatry lineshapes may be more appropriate in certain ranges of $\rho$ (i.e. high $\rho$).

These profiles, the Voight and Galatry lineshapes, are only significant if the experimental resolution is sufficient to observe asymmetry in the spectral lineshape, which results from a speed dependence of the collisional broadening coefficient $\gamma_{\rho,i,i-k}$. This speed-inhomogeneous asymmetry has also been shown to be important at high temperatures, but relatively unimportant at low temperatures (Hussong et al. 2000). A comprehensive discussion on the application of the various natural linewidths and lineshapes is presented by Murray and Javan (1972) and Rosasco and Hurst (1992).