APPENDIX

Raman cross-section

For Q-branch diagonal elements[1,2], S and O branch from[3]: α and γ are the invariants of the polarizability tensor. Only $\Delta v = 1$ transitions (which are the strongest). For $\alpha_{\parallel}$, i.e. parallel polarization of pump and probe:

$$\begin{aligned}
\left.\frac{\delta\sigma}{\delta\Omega}\right|_{\substack{v+1\leftarrow v\\ J-2\leftarrow J}} &= \frac{\hbar\omega_s^4}{2\omega_e c^4 M}\times\left(\frac{2}{15}b^O_{J,J}F^O_\gamma\gamma^2\right)(v+1) && \text{O}\\
\left.\frac{\delta\sigma}{\delta\Omega}\right|_{\substack{v+1\leftarrow v\\ J\leftarrow J}} &= \frac{\hbar\omega_s^4}{2\omega_e c^4 M}\times\left(F^Q_\alpha\alpha^2+\frac{4}{45}b^Q_{J,J}F^Q_\gamma\gamma^2\right)(v+1) && \text{Q}\\
\left.\frac{\delta\sigma}{\delta\Omega}\right|_{\substack{v+1\leftarrow v\\ J+2\leftarrow J}} &= \frac{\hbar\omega_s^4}{2\omega_e c^4 M}\times\left(\frac{2}{15}b^S_{J,J}F^S_\gamma\gamma^2\right)(v+1) && \text{S}
\end{aligned} \tag{1}$$

For $\alpha_{\perp}$, i.e. orthogonal polarization of pump and probe[1]:

$$\begin{aligned}
\left.\frac{\delta\sigma}{\delta\Omega}\right|_{\substack{v+1\leftarrow v\\ J-2\leftarrow J}} &= \frac{\hbar\omega_s^4}{2\omega_e c^4 M}\times\left(\frac{1}{10}b^O_{J',J}F^O_\gamma\gamma^2\right)(v+1) && \text{O}\\
\left.\frac{\delta\sigma}{\delta\Omega}\right|_{\substack{v+1\leftarrow v\\ J\leftarrow J}} &= \frac{\hbar\omega_s^4}{2\omega_e c^4 M}\times\left(\frac{1}{15}b^Q_{J',J}F^Q_\gamma\gamma^2\right)(v+1) && \text{Q}\\
\left.\frac{\delta\sigma}{\delta\Omega}\right|_{\substack{v+1\leftarrow v\\ J+2\leftarrow J}} &= \frac{\hbar\omega_s^4}{2\omega_e c^4 M}\times\left(\frac{1}{10}b^S_{J',J}F^S_\gamma\gamma^2\right)(v+1) && \text{S}
\end{aligned} \tag{2}$$

Where

$$F_\alpha\alpha^2 = \left\langle v,J|\alpha|v',J'\right\rangle^2, \quad F_\gamma\gamma^2 = \left\langle v,J|\gamma|v',J'\right\rangle^2 \tag{3}$$

from the definition of the Hermann-Wallis-Factors, which account for the branch dependent vibration-rotation interaction,[2] and the Placzek-Teller-coefficients (after some simple math from[1])

$$b^O_{J',J} = \frac{J(J-1)}{(2J-1)(2J+1)}, \quad b^Q_{J',J} = \frac{J(J+1)}{(2J-1)(2J+3)}, \quad b^S_{J',J} = \frac{(J+1)(J+2)}{(2J+3)(2J+1)} \tag{4}$$

for each branch.

After some transformations, the equation for the amplitudes of the resonant third order susceptibility **??** reads as follows:

$$a_q^{\parallel,\perp} = 10^{18}N\Delta_q(v+1)\frac{\zeta^2}{4\pi c}\begin{cases}
\frac{2}{15}\xi^2 b^O_{J,J}F^O_\gamma & \text{O}_\parallel\\
\frac{3}{4}\text{O}_\parallel & \text{O}_\perp\\
 & \\
(1+\frac{4}{45}\xi^2 b^Q_{J',J})F^Q & \text{Q}_\parallel\\
\frac{1}{15}\xi^2 b^Q_{J',J}F^Q & \text{Q}_\perp\\
 & \\
\frac{2}{15}\xi^2 b^S_{J,J}F^S_\gamma & \text{S}_\parallel\\
\frac{3}{4}\text{S}_\parallel & \text{S}_\perp
\end{cases} \tag{5}$$

where $\xi = \gamma/\alpha$ corresponds to AG in CARSFT[4], i.e. the ratio of the anisotropy of the polarizability derivative to the mean polarizability derivative and ζ is the mean polarizability derivative α divided by $\sqrt{2\pi c\omega_e M}$, corresponding to $AC1$. This was chosen to be compatible with the definitions in CARSFT's molecular parameter files[4]. Also: multiply by 10^{18} to have the same units as χ_{NR} in cars.mol. For these equations, $F^Q_\gamma = F^Q_\alpha = F^Q$[1].

The angles Φ and Θ denote the angle between pump and probe and the angle of a polarizer in front of the spectrometer.

$$a_q = cos(\Phi)cos(\Theta)a_q^{\parallel} + sin(\Phi)sin(\Theta)a_q^{\perp} \tag{6}$$

Hermann-Wallis-Factors

Judging from the list of references in[4], CARSFT originally uses the James-Klemperer-Model[1] for Q-branch HW-Factors and the Buckingham-Model for O- and S-Branches[3]. In addition to those implemented in CARSFT, other Q-branch HW factors have been implemented, see equation 8 (taken from[2], primary sources in equations).

$$F^O = \left(1 - 4\frac{B_e\gamma}{\omega_e\frac{\delta\gamma}{\delta r}r}(2J+3)\right)^2, \quad F^S = \left(1 - 4\frac{B_e}{\omega_e\frac{\delta\gamma}{\delta r}r}(2J-1)\right)^2 \tag{7}$$

$$\begin{aligned} F^Q_{JK} &= 1 - 3\eta J(J+1)/2 && \text{James et al.[1]} \\ F^Q_{LBY} &= \left[1 - 3\eta^2\left(a_1+1\right)J(J+1)/4\right]^2 && \text{Bouanich et al.[5]} \\ F^Q_{TB} &= 1 - \left[3\left(a_1+1\right)/2 - 4p_2/p_1\right]\eta^2 J(J+1)/4]^2 && \text{Tipping et al.[6]} \\ \text{where } \eta &= \frac{2B_e}{\omega_e} \end{aligned} \tag{8}$$

For HW factors other than James-Klemperer, S and O branch will still use Buckingham as the others do not provide corrections for these branches (which are not so significant in ro-vib cars anyway).

References

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[5] JP Bouanich, C Brodbeck, *J. Quant. Spectrosc. Radiat. Transfer* **1976**, *16* (2), 153–163.

[6] RH Tipping, JP Bouanich, *J. Quant. Spectrosc. Radiat. Transfer* **2001**, *71* (1), 99–103.