# Herman–Wallis Factors for Raman Transitions of $^1\Sigma$-State Diatomic Molecules

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**Accurate theoretical expressions for Herman–Wallis factors for the pure rotational, fundamental and first two overtone vibration–rotational bands have been derived. These are expressed for arbitrary rotational quantum numbers in terms of the Dunham potential parameters and the coefficients of a general operator represented by a power series expansion. The inclusion of higher order corrections in a consistent way reduces the discrepancy reported by previous workers for $H_2$ between results obtained numerically and analytically. The present expressions are of sufficient accuracy to enable one to obtain precise experimental values for the anisotropy of the polarizability and its derivatives from an analysis of Raman line intensities.**

## INTRODUCTION

In the past few years, several papers have been published[1–5] in which the relative intensities of O and S branch ($\Delta J = \pm 2$) vibration–rotational Raman lines for diatomic molecules have been analyzed in order to obtain values for the anisotropy of the polarizability and its derivatives with respect to internuclear separation. In order to carry out this analysis, one needs accurate theoretical expressions (or numerical values[3,5]) for the corresponding polarizability matrix elements, including the effects of vibration–rotation interaction (Herman–Wallis factors[6]). Analytical results for the dipole moment matrix elements and Herman–Wallis factors applicable to infrared spectra have been published,[7,8] and the purpose of this paper is to indicate how these results can be generalized to allow for arbitrary rotational selection rules and transition operators.

## THEORETICAL

We shall assume that the operator $P$ responsible for the absorption or scattering of radiation during a transition can be expanded about the equilibrium internuclear separation $R_e$ in terms of the reduced displacement:

$$x = \frac{R - R_e}{R_e} \tag{1}$$

that is

$$P(x) = \sum_{j=0} p_j x^j \tag{2}$$

For the O and S Raman lines, $P$ would correspond to the anisotropy of the polarizability $[\alpha_{\parallel}(R) - \alpha_{\perp}(R)]$, while for other applications it could equally well represent the isotropic polarizability, a multipole moment function, etc.

The Herman–Wallis factors are defined by

$$F_{vJ}^{v'J'} = \frac{\langle vJ|P(x)|v'J'\rangle^2}{\langle v0|P(x)|v'0\rangle^2} \tag{3}$$

where $v$ and $J$ denote the vibrational and rotational quantum numbers, respectively. James and Klemperer,[9] in an early paper that treated the effects of vibration–rotation interaction in Raman spectra, kept only the first two terms in the expansion [Eqn (2)] and calculated the matrix elements in Eqn (3) using analytical wavefunctions for a model potential energy function consisting of a harmonic oscillator term plus the first three terms in the expansion of the centrifugal potential $\hbar^2 J(J+1)/2\mu R^2$. They presented results for the pure rotational and fundamental vibrational bands expressed in terms of the small expansion parameter $\gamma = 2B_e/\omega_e$. Their results for the fundamental band, however, are incomplete in that there are additional terms to those which they reported of order $\gamma^2$. Because of the possibility of cancellation among the various contributions, the neglect of these terms can lead to significant discrepancies in some cases, for example, in $H_2$.[3,5]

Recently, we have derived extensive analytical results for wavefunctions, matrix elements and Herman–Wallis factors for the Dunham potential[10]

$$V(x) = \gamma^{-2} B_e x^2 \left(1 + \sum_{j=1} a_j x^j\right) \tag{4}$$

by means of computer algebra. Theoretical expressions for the Herman–Wallis factors for arbitrary rotational transitions for the pure rotational, fundamental and first two overtone vibration–rotational bands are presented in Table 1, in which we have introduced the following

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**Table 1. Herman–Wallis factors**

$$F_{0J}^{0J'}=\left[1+\gamma^2\left(\frac{\beta+\beta'}{2}\right)\nu_1\right]^2$$

$$F_{0J}^{1J'}=\left[1+\gamma\left(\frac{\beta'-\beta}{2}\right)\left(-2\theta_{\mathrm{o}}+\gamma\left[\left(-\frac{41}{8}a_1^2+\frac{9}{2}a_2-\frac{15}{2}a_1-6\right)\theta_{\mathrm{o}}+\left(\frac{13}{4}a_1+\frac{3}{4}\right)\theta_1-\theta_2\right]\right)+\gamma^2\left(\frac{\beta'+\beta}{2}\right)\left(-\frac{3}{4}(a_1+1)\theta_1+2\theta_2\right)\right]^2$$

$$\begin{aligned}F_{0J}^{2J'}=\Bigg[&1+\gamma\left(\frac{\beta'-\beta}{2}\right)\Bigg(\left(-\frac{a_1}{2}+\frac{3}{2}\right)\phi_{\mathrm{o}}-2\phi_1+\gamma\Bigg[\left(-\frac{333}{64}a_1^3+\frac{129}{16}a_1a_2-\frac{5}{2}a_3+\frac{279}{64}a_1^2-\frac{99}{16}a_2+9a_1+\frac{15}{2}\right)\phi_{\mathrm{o}}\\&+\left(-\frac{135}{16}a_1^2+\frac{37}{4}a_2-\frac{111}{8}a_1-10\right)\phi_1+\left(\frac{33}{4}a_1+\frac{9}{4}\right)\phi_2-3\phi_3\Bigg]\Bigg)\\&+\gamma^2\left(\frac{\beta'-\beta}{2}\right)^2 2\phi_{\mathrm{o}}+\gamma^2\left(\frac{\beta'+\beta}{2}\right)\left(\left(-\frac{9}{4}a_1^2+2a_2-\frac{9}{4}a_1-2\right)\phi_1+\left(-\frac{a_1}{2}-\frac{3}{2}\right)\phi_2+3\phi_3\right)\Bigg]^2\end{aligned}$$

$$\begin{aligned}F_{0J}^{3J'}=\Bigg[&1+\gamma\left(\frac{\beta'-\beta}{2}\right)\Bigg(\left(-\frac{a_1^2}{8}-\frac{a_2}{6}+a_1-\frac{4}{3}\right)\mu_{\mathrm{o}}+\frac{3}{2}(-a_1+1)\mu_1-2\mu_2\\&+\gamma\Bigg[\left(-\frac{363}{128}a_1^4+\frac{37}{16}a_1^2a_2+\frac{3}{8}a_1a_3+\frac{17}{8}a_2^2-\frac{5}{4}a_4+\frac{57}{4}a_1^3-24a_1a_2+7a_3-a_1^2+8a_2-10a_1-10\right)\mu_{\mathrm{o}}\\&+\left(-\frac{717}{32}a_1^3+\frac{283}{8}a_1a_2-\frac{39}{4}a_3-\frac{69}{32}a_1^2-\frac{81}{8}a_2+\frac{17}{2}a_1+\frac{45}{4}\right)\mu_1+\left(-7a_1^2+\frac{44}{3}a_2-\frac{41}{2}a_1-\frac{44}{3}\right)\mu_2+\frac{9}{2}(3a_1+1)\mu_3-6\mu_4\Bigg]\Bigg)\\&+\gamma^2\left(\frac{\beta'-\beta}{2}\right)^2\left[\left(a_1-3\right)\mu_{\mathrm{o}}+2\mu_1\right]+\gamma^2\left(\frac{\beta'+\beta}{2}\right)\Bigg(\left(-\frac{99}{64}a_1^3+\frac{3}{16}a_1a_2+\frac{5}{4}a_3-\frac{99}{64}a_1^2-\frac{21}{16}a_2-\frac{3}{2}a_1+\frac{5}{4}\right)\mu_1+\left(-\frac{39}{8}a_1^2+\frac{9}{2}a_2-\frac{21}{4}a_1-4\right)\mu_2\\&+\frac{3}{4}(a_1-3)\mu_3+4\mu_4\Bigg)\Bigg]^2\end{aligned}$$

notation:

$$\nu_i\equiv\frac{p_i}{\langle 00|P(x)|00\rangle}\approx\frac{p_i}{p_{\mathrm{o}}}\tag{5}$$

$$\theta_i\equiv\frac{\sqrt{\gamma}p_i}{\sqrt{2}\langle 00|P(x)|10\rangle}$$

$$\approx\frac{p_i}{p_1+\gamma\left[\left(\frac{11}{16}a_1^2-\frac{3}{4}a_2\right)p_1-\frac{5}{2}a_1p_2+\frac{3}{2}p_3\right]}$$

$$\phi_i\equiv\frac{\gamma p_i}{\sqrt{2}\langle 00|P(x)|20\rangle}$$

$$\approx\frac{p_i}{\left(p_2+\frac{a_1p_1}{2}\right)+\gamma\left[\left(\frac{243}{64}a_1^3-\frac{111}{16}a_1a_2+\frac{5}{2}a_3\right)p_1+\left(\frac{3}{32}a_1^2-\frac{15}{8}a_2\right)p_2-\frac{9}{2}a_1p_3+3p_4\right]}$$

$$\mu_i\equiv\frac{\sqrt{3}\gamma^{3/2}p_i}{2\langle 00|P(x)|30\rangle}$$

$$\approx\frac{p_i}{\left[p_3+a_1p_2+\left(\frac{3a_1^2}{16}+\frac{a_2}{4}\right)p_1\right]+\gamma\left[\left(\frac{909}{256}a_1^4-\frac{123}{32}a_1^2a_2-\frac{9}{16}a_1a_3-\frac{39}{16}a_2^2+\frac{15}{8}a_4\right)p_1+\left(\frac{21}{2}a_1^3-21a_1a_2+7a_3\right)p_2+\left(-3a_1^2-3a_2\right)p_3-6a_1p_4+5p_5\right]}$$

and

$$\beta=J(J+1)$$

In the previous infrared work,[7,8,10] the rotational dependence was expressed in terms of the running index:

$$m=\frac{\beta'-\beta}{2}\tag{6}$$

and the Herman–Wallis factors were written in the form

$$F_{vJ}^{v'J'}=1+C_v^{v'}m+D_v^{v'}m^2+\cdots\tag{7}$$

However, one has to be careful in applying the latter results directly to Raman transitions, for the following reason. After multiplying out the expressions in Table 1, the terms proportional to $\gamma^2$ have a rotational dependence characterized by either $[(\beta'-\beta)/2]^2$ or $(\beta'+\beta)/2$. For $\Delta J=\pm 1$ transitions (R and P branches, respectively), both of these factors can be written as $m^2$, but this is obviously not true for other rotational selection rules, as can be seen from the interrelationships among the rotational variables given in Table 2. By including the $\gamma^2$ contributions consistently, the differences reported by previous workers[3,5] between results obtained numerically and through analytical formulae[9] are greatly reduced; this is illustrated by sample calculations in the following section.

**Table 2. Interrelationships among the rotational variables for different branches**

| Rotational Variable | Branch O | P | Q | R | S |
|---|---|---|---|---|---|
| $J'$ | $J-2$ | $J-1$ | $J$ | $J+1$ | $J+2$ |
| $m$ | $-2J+1$ | $-J$ | 0 | $J+1$ | $2J+3$ |
| $\left(\frac{\beta'-\beta}{2}\right)$ | $m$ | $m$ | 0 | $m$ | $m$ |
| | $-2J+1$ | $-J$ | 0 | $J+1$ | $2J+3$ |
| $\left(\frac{\beta'+\beta}{2}\right)$ | $(m^2+3)/4$ | $m^2$ | — | $m^2$ | $(m^2+3)/4$ |
| | $J^2-J+1$ | $J^2$ | $J^2+J$ | $J^2+2J+1$ | $J^2+3J+3$ |

## APPLICATION TO $H_2$

In order to compare the accuracy of the present results with that of results calculated with previously published analytical expressions[1,9] and by numerical integration,[5] it is convenient to consider the ratio of intensities of the S and O fundamental branch lines originating from the same initial state. This ratio is proportional to the quantity $G_{01}$, where

$$G_{01}(J) \equiv \frac{\langle 0J|P|1J+2\rangle^2}{\langle 0J|P|1J-2\rangle^2} = \frac{F_{0\,J}^{1\,J+2}}{F_{0\,J}^{1\,J-2}} \tag{8}$$

(this ratio is also useful for analyzing experimental data as the statistical population factors would cancel).

The Dunham potential constants for $H_2$ as reported by Beckel and Wu[11] are listed in Table 3, together with the expansion coefficients, $p_i$, obtained through a least-squares fit of the *ab initio* anisotropic polarizability function (at 4880 Å) calculated by Cheung *et al.*[5] Using these data and the fundamental $F_{0J}^{1J'}$ expression listed in Table 1, we obtain the values for $G_{01}$ presented in column 4 in Table 4. Also shown are the analytical results obtained by retaining only the lowest order rotational term ($[-2\gamma(\beta'-\beta)\theta_o]$, denoted as 'first-order') and by use of the equation published by James and Klemperer.[9]

**Table 3. Potential[a] and polarizability[b] (4880 Å) coefficients for $H_2$**

| | |
|---|---|
| $a_1=-1.6029$ | $p_0=1.91633$ |
| $a_2=1.865$ | $p_1=4.93862$ |
| $a_3=-1.999$ | $p_2=3.29358$ |
| $a_4=2.05$ | $p_3=2.21407$ |
| $a_5=-2.0$ | $\gamma=2.76528\times10^{-2}$ |

[a] Ref. 11.
[b] Ref. 5.

**Table 4. Comparison between analytical and numerical values for the ratio $G_{01}(J)$ for $H_2$**

| $J$ | Analytical results: First-order[a] | James and Klemperer[b] | Present results, second-order | Numerical results[c] |
|---|---|---|---|---|
| 2 | 0.6204 | 0.6364 | 0.6399 | 0.6482 |
| 3 | 0.5109 | 0.5285 | 0.5365 | 0.5452 |
| 4 | 0.4195 | 0.4366 | 0.4509 | 0.4588 |
| 5 | 0.3429 | 0.3582 | 0.3801 | 0.3862 |
| 6 | 0.2788 | 0.2912 | 0.3216 | 0.3251 |
| 7 | 0.2251 | 0.2339 | 0.2733 | 0.2736 |
| 8 | 0.1803 | 0.1851 | 0.2335 | 0.2302 |
| 9 | 0.1428 | 0.1437 | 0.2007 | 0.1934 |
| 10 | 0.1117 | 0.1087 | 0.1735 | 0.1622 |

[a] Ref. 1. First-order indicates that only the leading term proportional to $\gamma(\beta'-\beta)$ is retained.
[b] Ref. 9. The slightly different values reported in Ref. 5 arise from slightly different magnitudes for $p_0$ and $p_1$ assumed.
[c] Ref. 5.

As can be seen by comparison with the accurate results obtained via direct numerical integration,[5] the inclusion of the $\gamma^2$ terms improves the agreement between the analytical and numerical results. On the other hand, the inclusion of only the harmonic second-order terms[9] ($a_j = 0$ and $p_2 = p_3 = 0$) improves the agreement for low $J$, but eventually leads to larger discrepancies than without these corrections. Similar results would be expected for the overtone bands, and for other molecules.[12] However, since the magnitude of $\gamma$ for $H_2$ is larger than for other typical diatomic molecules, the discrepancies between the different analytical expressions would be concomitantly smaller. In any event, the accuracy of the Herman–Wallis expressions given in Table 1 should provide sufficient accuracy for the theoretical interpretation of most Raman intensity measurements.

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