

## RESEARCH NOTE

*Line strengths for fine- and hyperfine-resolved electric-quadrupole rotation-vibration transitions in Hund's case b molecules*M. Germann<sup>a</sup> and S. Willitsch<sup>a\*</sup><sup>a</sup>*Department of Chemistry, University of Basel, Klingelbergstrasse 80, 4056 Basel, Switzerland;  
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We report the derivation of line-strength formulae for fine- and hyperfine resolved electric-quadrupole rotation-vibration transitions in Hund's case b molecules using the formalism of spherical tensor algebra. These expressions may serve in the analysis of spectra of linear molecules, in particular diatomic molecules such as H<sub>2</sub>, N<sub>2</sub> and their ions, which are of current interest in precision spectroscopy.

**Keywords:** forbidden transitions, hyperfine structure, quadrupole spectra, precision spectroscopy, molecular ions, Hönl-London factors

Recent progress towards spectroscopic precision experiments on molecules has rekindled interest in the study of dipole-forbidden molecular spectra. Such forbidden transitions exhibit very narrow natural linewidths which are desirable for very-high resolution experiments. In several recent publications, electric-dipole-forbidden vibrational transitions in homonuclear diatomics, i.e., electric-quadrupole transitions, have been identified as promising candidates for precision spectroscopic experiments [1–3]. While such transitions had been observed in selected neutral diatomics like H<sub>2</sub>, N<sub>2</sub> and O<sub>2</sub> already several decades ago [4–6], their observation in a molecular ion has only recently been achieved [7, 8].

The analysis of high-resolution quadrupole spectra requires expressions for the transition line strengths taking into account the fine and hyperfine structure. To the best of our knowledge, their derivation has not been reported before. Here, we derive expressions for the line strengths of fine- and hyperfine-resolved quadrupole rotation-vibration transitions in a Hund's case b<sub>*β*</sub> molecule [9] using spherical-tensor algebra [10]. These may be applied to, e.g., the vibrational spectra of the X <sup>2</sup>Σ<sub>g</sub><sup>+</sup> electronic ground states of H<sub>2</sub><sup>+</sup> and N<sub>2</sub><sup>+</sup> which are of particular interest for precision measurements [1–3, 7].

Fig. 1 shows energy levels and the angular-momentum-coupling hierarchy for a molecule in Hund's case b<sub>*β*</sub>, as is approximately the case for the X <sup>2</sup>Σ<sub>g</sub><sup>+</sup> ground electronic state of N<sub>2</sub><sup>+</sup> [11]. In this scheme, the total electron spin **S** couples to the total angular momentum without spin **N** yielding **J** (spin-rotation or fine structure). **J** then couples with the total nuclear spin **I** yielding the total angular momentum **F** (hyperfine structure). The molecular states can be denoted

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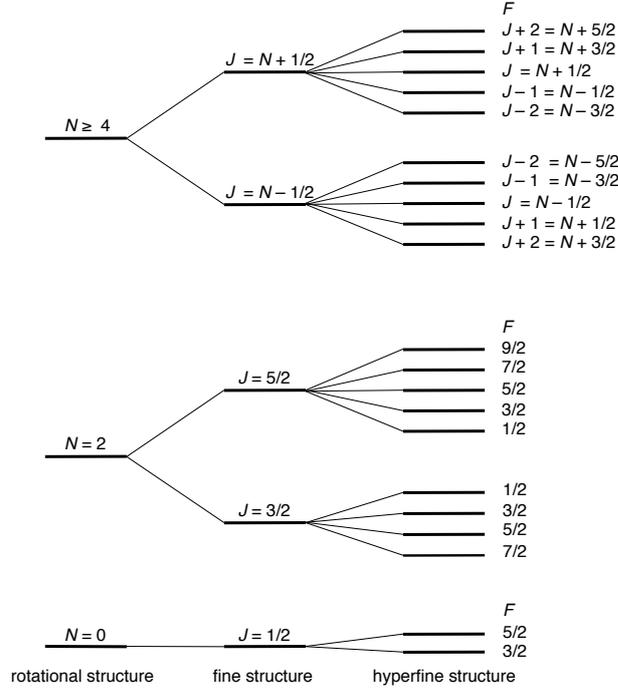


Figure 1. Energy levels and angular-momentum-coupling hierarchy for a Hund's case  $b_{\beta_J}$  molecule exemplified with ortho- $N_2^+$  (even rotational quantum numbers  $N$  associated with the nuclear spin quantum numbers  $I = 0, 2$ ) in its  $X^2\Sigma_g^+$  ground electronic state. See text for discussion.

as  $|n\Lambda\rangle|v\rangle|N\Lambda S J I F M_F\rangle$  where  $n$  labels the electronic state of the molecule,  $v$  stands for the vibrational quantum number and  $\Lambda$  is the quantum number of the projection of the electronic orbital angular momentum on the internuclear axis.  $N$  denotes the quantum number of the molecule's total angular momentum without spin (corresponding to the mechanical rotation of the molecule in a  $\Sigma$  electronic state).  $S$  is the total electron spin quantum number ( $S = 1/2$  for  $N_2^+ X^2\Sigma_g^+$ ),  $J$  the quantum number for the total angular momentum without nuclear spin,  $I$  the quantum number for the total nuclear spin, and finally  $F$  and  $M_F$  the total angular momentum quantum number and its associated space-fixed projection quantum number, respectively.

The line strength for a hyperfine-resolved electric-quadrupole rotation-vibration transition is then given by:

$$S_{n\Lambda}^{(\text{hfs})} = \sum_{M_F', M_F''} \sum_{p=-2}^2 \left| \left\langle n\Lambda, v', N'\Lambda S' J' I' F' M_F' \left| T_p^2 \left[ \hat{Q}^{(s)} \right] \right| n\Lambda, v'', N''\Lambda S'' J'' I'' F'' M_F'' \right\rangle \right|^2, \quad (1)$$

where  $''$  and  $'$  denote the lower and upper states of the transition, respectively.  $T_p^2 \left[ \hat{Q}^{(s)} \right]$  is the space-fixed electric-quadrupole operator in spherical tensor notation [12].

We express  $T_p^2 \left[ \hat{Q}^{(s)} \right]$  in terms of molecule-fixed coordinates

$$T_p^2 \left[ \hat{Q}^{(s)} \right] = \sum_{q=-2}^2 \left[ \mathcal{D}_{pq}^{(2)} \right]^* T_q^2 \left[ \hat{Q}^{(m)} \right], \quad (2)$$

where  $\mathcal{D}_{pq}^{(2)}$  is a second-rank Wigner rotation-matrix element [10] and the index (m) refers to the molecule-fixed frame. As the molecule-fixed electric-quadrupole operator does not act on the angular coordinates, we can separate the matrix element according to:

$$\begin{aligned} & \left\langle n\Lambda, v', N'\Lambda S' J' I' F' M'_F \left| \mathbb{T}_p^2 \left[ \hat{\mathbf{Q}}^{(s)} \right] \right| n\Lambda, v'', N''\Lambda S'' J'' I'' F'' M''_F \right\rangle \\ &= \sum_{q=-2}^2 \left\langle n\Lambda, v' \left| \mathbb{T}_q^2 \left[ \hat{\mathbf{Q}}^{(m)} \right] \right| n\Lambda, v'' \right\rangle \left\langle N'\Lambda S' J' I' F' M'_F \left| \left[ \mathcal{D}_{pq}^{(2)} \right]^* \right| N''\Lambda S'' J'' I'' F'' M''_F \right\rangle. \end{aligned} \quad (3)$$

Using the Wigner-Eckart theorem, the spin-rotational matrix element is expressed as

$$\begin{aligned} & \left\langle N'\Lambda S' J' I' F' M'_F \left| \left[ \mathcal{D}_{pq}^{(2)} \right]^* \right| N''\Lambda S'' J'' I'' F'' M''_F \right\rangle \\ &= (-1)^{F'-M'_F} \begin{pmatrix} F' & 2 & F'' \\ -M'_F & p & M''_F \end{pmatrix} \left\langle N'\Lambda S' J' I' F' \parallel \left[ \mathcal{D}_{\cdot q}^{(2)} \right]^* \parallel N''\Lambda S'' J'' I'' F'' \right\rangle, \end{aligned} \quad (4)$$

where on the right-hand side the expression in pointed brackets is a reduced matrix element and the expression in round brackets a Wigner  $3j$ -symbol [10]. As the rotation-matrix elements do not act on the nuclear spin, the angular momenta  $I$  and  $F$  can be eliminated from the reduced matrix element [10]:

$$\begin{aligned} & \left\langle N'\Lambda S' J' I' F' \parallel \left[ \mathcal{D}_{\cdot q}^{(2)} \right]^* \parallel N''\Lambda S'' J'' I'' F'' \right\rangle \\ &= \delta_{I'I''} (-1)^{J'+I'+F''+2} \sqrt{2F'+1} \sqrt{2F''+1} \left\{ \begin{matrix} J' & F' & I' \\ F'' & J'' & 2 \end{matrix} \right\} \left\langle N'\Lambda S' J' \parallel \left[ \mathcal{D}_{\cdot q}^{(2)} \right]^* \parallel N''\Lambda S'' J'' \right\rangle, \end{aligned} \quad (5)$$

where the expression in curly brackets denotes a Wigner  $6j$ -symbol. Similarly, the resulting reduced matrix element can further be simplified by eliminating the quantum numbers  $S$  and  $J$ :

$$\begin{aligned} & \left\langle N'\Lambda S' J' \parallel \left[ \mathcal{D}_{\cdot q}^{(2)} \right]^* \parallel N''\Lambda S'' J'' \right\rangle \\ &= \delta_{S'S''} (-1)^{N'+S'+J''+2} \sqrt{2J'+1} \sqrt{2J''+1} \left\{ \begin{matrix} N' & J' & S' \\ J'' & N'' & 2 \end{matrix} \right\} \left\langle N'\Lambda \parallel \left[ \mathcal{D}_{\cdot q}^{(2)} \right]^* \parallel N''\Lambda \right\rangle. \end{aligned} \quad (6)$$

The remaining reduced matrix element can be expressed as [12]:

$$\left\langle N'\Lambda \parallel \left[ \mathcal{D}_{\cdot q}^{(2)} \right]^* \parallel N''\Lambda \right\rangle = (-1)^{N'-\Lambda} \sqrt{2N'+1} \sqrt{2N''+1} \begin{pmatrix} N' & 2 & N'' \\ -\Lambda & q & \Lambda \end{pmatrix}. \quad (7)$$

Only the term with  $q = 0$  contributes to the sum in Eq. (3) because of the properties of the Wigner  $3j$ -symbol in Eq. (7).

Substituting equations (4) to (7) into (3), we obtain the matrix element

$$\begin{aligned}
 & \left\langle n\Lambda, v', N' \Lambda S' J' I' F' M'_F \left| \mathbb{T}_p^2 \left[ \hat{Q}^{(s)} \right] \right| n\Lambda, v'', N'' \Lambda S'' J'' I'' F'' M''_F \right\rangle \\
 &= \delta_{S'S''} \delta_{I'I''} (-1)^{S'+I'+J'+J''+F'+F''-M'_F-\Lambda} \sqrt{2N'+1} \sqrt{2N''+1} \sqrt{2J'+1} \sqrt{2J''+1} \\
 & \quad \sqrt{2F'+1} \sqrt{2F''+1} \begin{pmatrix} N' & 2 & N'' \\ -\Lambda & 0 & \Lambda \end{pmatrix} \begin{pmatrix} F' & 2 & F'' \\ -M'_F & p & M''_F \end{pmatrix} \\
 & \quad \left\{ \begin{matrix} N' & J' & S' \\ J'' & N'' & 2 \end{matrix} \right\} \left\{ \begin{matrix} J' & F' & I' \\ F'' & J'' & 2 \end{matrix} \right\} \left\langle n\Lambda, v' \left| \mathbb{T}_0^2 \left[ \hat{Q}^{(m)} \right] \right| n\Lambda, v'' \right\rangle.
 \end{aligned} \tag{8}$$

The line strength for a hyperfine-resolved electric-quadrupole rotation-vibration line is thus

$$\begin{aligned}
 S_{n\Lambda, v' N' S' J' I' F' / v'' N'' S'' J'' I'' F''}^{(\text{hfs})} &= \delta_{S'S''} \delta_{I'I''} (2N'+1)(2N''+1)(2J'+1)(2J''+1)(2F'+1)(2F''+1) \\
 & \quad \begin{pmatrix} N' & 2 & N'' \\ -\Lambda & 0 & \Lambda \end{pmatrix}^2 \left\{ \begin{matrix} N' & J' & S' \\ J'' & N'' & 2 \end{matrix} \right\}^2 \left\{ \begin{matrix} J' & F' & I' \\ F'' & J'' & 2 \end{matrix} \right\}^2 \\
 & \quad \left| \left\langle n\Lambda, v' \left| \mathbb{T}_0^2 \left[ \hat{Q}^{(m)} \right] \right| n\Lambda, v'' \right\rangle \right|^2,
 \end{aligned} \tag{9}$$

where the orthogonality properties of the 3j-symbols have been used for simplification [10]. In the double-harmonic approximation [13], the vibrational matrix element appearing in the last line of Eq. (9) may be evaluated as [14]

$$\left\langle n\Lambda, v' \left| \mathbb{T}_0^2 \left[ \hat{Q}^{(m)} \right] \right| n\Lambda, v'' \right\rangle \approx \sqrt{\frac{3}{2}} \frac{dQ_{n,zz}^{(m)}}{dR} \Big|_{R=R_e} R_e \sqrt{\frac{\tilde{B}_e}{\tilde{\omega}_e}} \sqrt{v''+1}, \tag{10}$$

where  $Q_{n,zz}^{(m)}$  is the  $zz$ -component of the Cartesian electric quadrupole-moment tensor of the molecule in the electronic state  $n$ ,  $R$  the internuclear distance,  $R_e$  its equilibrium value and  $\tilde{B}_e$  and  $\tilde{\omega}_e$  the rotational constant and vibrational frequency in units of wavenumbers, respectively.

From the Kronecker deltas and the properties of the 3j- and 6j-symbols in Eq. (9), the following selection rules are obtained:

$$\Delta S = S' - S'' = 0, \tag{11}$$

$$\Delta I = I' - I'' = 0, \tag{12}$$

$$\Delta F = F' - F'' = 0, \pm 1, \pm 2 \tag{13}$$

$$\Delta J = J' - J'' = 0, \pm 1, \pm 2 \tag{14}$$

$$\Delta N = N' - N'' = 0, \pm 1, \pm 2. \tag{15}$$

For  $\Lambda = 0$ , the cases  $\Delta N = \pm 1$  and  $N' = N'' = 0$  are forbidden. The angular part of Eq. (9) can readily be evaluated with a computer algebra system such as “Mathematica” [15]. An application is illustrated in Fig. 2 which shows the normalized line strengths of the most intense hyperfine transitions in descending order for (a) a S(0) and (b) a S(6) transition. S denotes the  $\Delta N = +2$  branch and the number in parentheses refers to the value of  $N''$ . One can see that for higher values of  $N''$  as in Fig. 2 (b), a propensity rule  $\Delta N = \Delta J = \Delta F$  emerges because

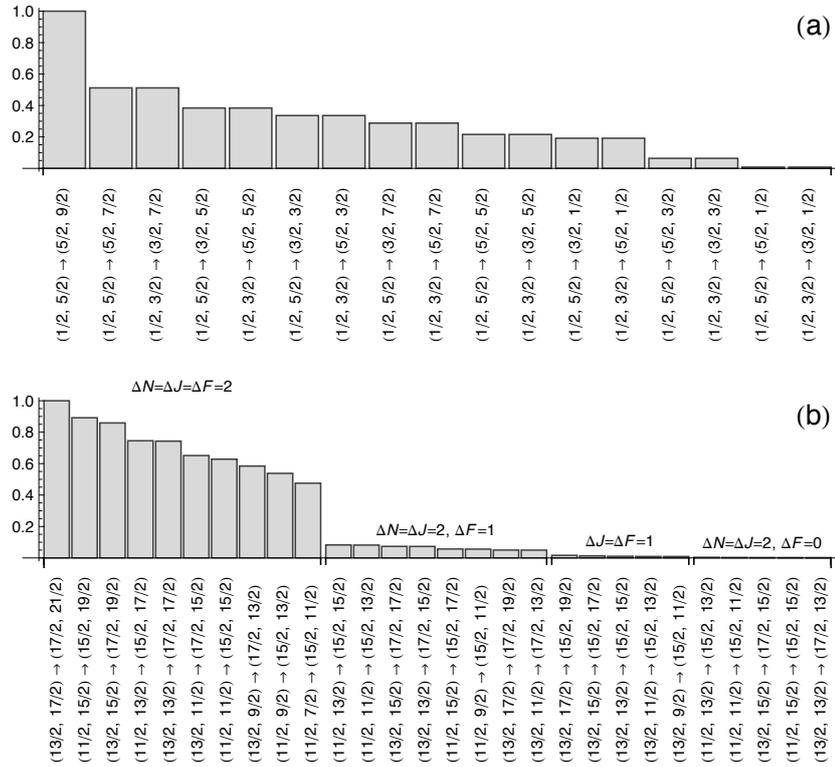


Figure 2. Normalized line strengths of hyperfine components of (a) S(0) and (b) S(6) quadrupole rotation-vibration transitions. In the case of higher values of  $N''$ , as in (b), note the emergence of a  $\Delta N = \Delta J = \Delta F$  propensity rule. Transitions are labeled as  $(J'', F'') \rightarrow (J', F')$ .

of angular-momentum uncoupling. Similar effects have been observed previously, for instance, in electric-dipole-allowed hyperfine-resolved electronic spectra of  $N_2^+$  [16].

If only the fine- but not the hyperfine structure is resolved, an analogous derivation yields the result for the line strength of fine-structure components:

$$S_{n\Lambda}^{(fs)} = \delta_{S' S''} g_{\text{ns}} (2N' + 1)(2N'' + 1)(2J' + 1)(2J'' + 1) \left( \begin{matrix} N' & 2 & N'' \\ -\Lambda & 0 & \Lambda \end{matrix} \right)^2 \left\{ \begin{matrix} N' & J' & S' \\ J'' & N'' & 2 \end{matrix} \right\}^2 \left| \langle n\Lambda, v' | T_0^2 [\hat{Q}^{(m)}] | n\Lambda, v'' \rangle \right|^2, \quad (16)$$

where  $g_{\text{ns}}$  is the nuclear-spin statistical weight factor. This result can be compared with the equivalent expression for a Hund's case a molecule reported in Ref. [17]. Eq. (16) also reproduces the line strengths of the quadrupole infrared transitions of  $O_2$  calculated for Hund's case b in Ref. [18]. For reference, we list in Tab. 1 the spin-rotational line strength factors (“Hönl-London factors”) obtained from the evaluation of the angular terms in Eq. 16. Note the emergence of a  $\Delta N = \Delta J$  propensity rule for high values of  $N$ , which is evident from the scaling with  $N''$  of the line strength factors given in Tab. 1.

In the present research note, we have reported the derivation of line-strength formulae for fine- and hyperfine-resolved electric-quadrupole rotation-vibration transitions for the Hund's case  $b_{\beta_j}$  coupling scheme. These expressions may serve in the analysis of the vibrational spectra of molecules such as  $H_2^+$  and  $N_2^+$  of relevance for precision spectroscopic measurements. Eq. (9) can also be applied to other Hund's cases after a suitable basis transformation as outlined in, e.g., Ref. [12]. The present expressions can also readily be adapted to mixed coupling cases as are found, for

Table 1. Spin-rotational line strength factors for electric-quadrupole rotation-vibration lines in a  $^2\Sigma$  state.  $F_1$  and  $F_2$  refer to the spin-rotation components  $J = N + 1/2$  and  $J = N - 1/2$ , respectively (see Fig. 1).

Component	$\Delta N = -2$	$\Delta N = 0$	$\Delta N = +2$
$F_1'' \rightarrow F_1'$	$\frac{3N''(N''-1)(N''+1)}{(2N''-1)(2N''+1)}$	$\frac{2N''(N''+1)(N''+2)}{(2N''+1)(2N''+3)}$	$\frac{3(N''+1)(N''+2)(N''+3)}{(2N''+3)(2N''+5)}$
$F_1'' \rightarrow F_2'$	0	$\frac{6N''(N''+1)}{(2N''-1)(2N''+1)(2N''+3)}$	$\frac{6(N''+1)(N''+2)}{(2N''+1)(2N''+3)(2N''+5)}$
$F_2'' \rightarrow F_1'$	$\frac{6N''(N''-1)}{(2N''-3)(2N''-1)(2N''+1)}$	$\frac{6N''(N''+1)}{(2N''-1)(2N''+1)(2N''+3)}$	0
$F_2'' \rightarrow F_2'$	$\frac{3N''(N''-2)(N''-1)}{(2N''-3)(2N''-1)}$	$\frac{2N''(N''-1)(N''+1)}{(2N''-1)(2N''+1)}$	$\frac{3N''(N''+1)(N''+2)}{(2N''+1)(2N''+3)}$

instance, in low rotational levels of  $N_2^+$  [19].

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