Derivation of the relationship between Hund's case (a) and base (b) vibronic matrix elements

We start with the following three relationships discussed in the text. These are the general relationship for Hund's case (a) matrix elements in terms of Hund's case (b) matrix elements:

$$\begin{aligned}
&\langle \eta v'\Lambda'; S'\Sigma'; J'M\Omega' | \hat{H} | \eta v\Lambda; S\Sigma; JM\Omega \rangle \\
&= \sum_{N,N'} (-1)^{N'-N+S'-S+\Omega'-\Omega} \sqrt{(2N+1)(2N'+1)} \begin{pmatrix} J' & S' & N' \\ \Omega' & -\Sigma' & -\Lambda' \end{pmatrix} \begin{pmatrix} J & S & N \\ \Omega & -\Sigma & -\Lambda \end{pmatrix} \langle \eta v'\Lambda'; N'\Lambda' S' JM | \hat{H} | \eta v\Lambda; N\Lambda SJM \rangle
\end{aligned} \tag{1}$$

the matrix element of the transition dipole using a Hund's case (a) basis:

$$\begin{aligned}
&\langle \eta' v'\Lambda; S\Sigma'; J'M'\Omega' | T_p^k(\mu) | \eta v\Lambda; S\Sigma; JM\Omega \rangle \\
&= \sum_q (-1)^{M'-\Omega'} \sqrt{(2J'+1)(2J+1)} \begin{pmatrix} J' & k & J \\ -\Omega' & q & \Omega \end{pmatrix} \begin{pmatrix} J' & k & J \\ -M' & p & M \end{pmatrix} \langle \eta' v'\Lambda'; S\Sigma' | T_q^k(\mu; J'\Omega' J\Omega) | \eta v\Lambda; S\Sigma \rangle
\end{aligned} \tag{2}$$

and the corresponding expression in Hund's case (b):

$$\begin{aligned}
&\langle \eta' v'\Lambda'; N'SJ'M' | T_p^k(\mu) | \eta v\Lambda; NSJM \rangle \\
&= (-1)^{J'-M'} \begin{pmatrix} J' & k & J \\ -M' & p & M \end{pmatrix} (-1)^{N'+S+J+k} \sqrt{(2J'+1)(2J+1)} \begin{Bmatrix} N' & J' & S \\ J & N & k \end{Bmatrix} \\
&\times \sum_q (-1)^{N'-\Lambda'} \sqrt{(2N'+1)(2N+1)} \begin{pmatrix} N' & k & N \\ -\Lambda' & q & \Lambda \end{pmatrix} \langle \eta' v'\Lambda' | T_q^k(\mu; N'N) | \eta v\Lambda \rangle
\end{aligned} \tag{3}$$

For more details on these expressions see Brown and Carrington (2003).

To relate the two vibronic dipole moments we substitute the latter two equations into both sides of the first, giving:

$$\begin{aligned}
&\sum_q (-1)^{M'-\Omega'} \sqrt{(2J'+1)(2J+1)} \begin{pmatrix} J' & k & J \\ -\Omega' & q & \Omega \end{pmatrix} \begin{pmatrix} J' & k & J \\ -M' & p & M \end{pmatrix} \langle \eta' v'\Lambda' | T_q^k(\mu; J'\Omega' J\Omega) | \eta v\Lambda \rangle \\
&= \sum_{N,N'} (-1)^{N'-N+\Omega'-\Omega} \sqrt{(2N+1)(2N'+1)} \begin{pmatrix} J' & S & N' \\ \Omega' & -\Sigma' & -\Lambda' \end{pmatrix} \begin{pmatrix} J & S & N \\ \Omega & -\Sigma & -\Lambda \end{pmatrix} \\
&\times (-1)^{J'-M'} \begin{pmatrix} J' & k & J \\ -M' & p & M \end{pmatrix} (-1)^{N'+S+J+k} \sqrt{(2J'+1)(2J+1)} \begin{Bmatrix} N' & J' & S \\ J & N & k \end{Bmatrix} \\
&\times \sum_q (-1)^{N'-\Lambda'} \sqrt{(2N'+1)(2N+1)} \begin{pmatrix} N' & k & N \\ -\Lambda' & q & \Lambda \end{pmatrix} \langle \eta' v'\Lambda' | T_q^k(\mu; N'N) | \eta v\Lambda \rangle
\end{aligned} \tag{4}$$

In making this substitution we have imposed the constraint that $S = S'$ but, in contrast to the previous version of this derivation, we have not required $\Sigma = \Sigma'$. (The derivation of equation (3) assumes $S = S'$, imposing this constraint on the transformation equation (1).) The terms in M, and some others factorise out of the sums on both sides leading to the simplified form:

$$
\begin{aligned}
&\sum_q (-1)^{J'-\Omega'} \begin{pmatrix} J' & k & J \\ -\Omega' & q & \Omega \end{pmatrix} \left\langle \eta' v' \Lambda'; S\Sigma' \middle| T_q^k(\mu; J'\Omega' J\Omega) \middle| \eta v \Lambda; S\Sigma \right\rangle \\
&= \sum_{N,N'} (-1)^{N'-N+\Omega'-\Omega} (2N+1)(2N'+1) \begin{pmatrix} J' & S & N' \\ \Omega' & -\Sigma' & -\Lambda' \end{pmatrix} \begin{pmatrix} J & S & N \\ \Omega & -\Sigma & -\Lambda \end{pmatrix} \\
&\times (-1)^{N'+S+J+k} \begin{Bmatrix} N' & J' & S \\ J & N & k \end{Bmatrix} \times \sum_q (-1)^{N'-\Lambda'} \begin{pmatrix} N' & k & N \\ -\Lambda' & q & \Lambda \end{pmatrix} \left\langle \eta' v' \Lambda' \middle| T_q^k(\mu; N'N) \middle| \eta v \Lambda \right\rangle
\end{aligned} \tag{5}
$$

For a given Ω' and Ω, the 3-*j* symbol means that there will be at most one non-zero term in the sum over *q* on the left hand side, so the sum can be replaced with a single term with $q = \Omega' - \Omega$. Similarly, for a given Λ' and Λ, only one term can contribute to the sum over *q* on the right hand side, with $q = \Lambda' - \Lambda$. This gives:

$$
\begin{aligned}
&(-1)^{J'-\Omega'} \begin{pmatrix} J' & k & J \\ -\Omega' & \Omega'-\Omega & \Omega \end{pmatrix} \left\langle \eta' v' \Lambda'; S\Sigma' \middle| T_{\Omega'-\Omega}^k(\mu; J'\Omega' J\Omega) \middle| \eta v \Lambda; S\Sigma \right\rangle \\
&= \sum_{N,N'} (-1)^{N'-N+\Omega'-\Omega+S+J+\Lambda'+k} (2N+1)(2N'+1) \begin{pmatrix} J' & S & N' \\ \Omega' & -\Sigma' & -\Lambda' \end{pmatrix} \begin{pmatrix} J & S & N \\ \Omega & -\Sigma & -\Lambda \end{pmatrix} \\
&\times \begin{Bmatrix} N' & J' & S \\ J & N & k \end{Bmatrix} \begin{pmatrix} N' & k & N \\ -\Lambda' & \Lambda'-\Lambda & \Lambda \end{pmatrix} \left\langle \eta' v' \Lambda' \middle| T_{\Lambda'-\Lambda}^k(\mu; N'N) \middle| \eta v \Lambda \right\rangle
\end{aligned} \tag{6}
$$

which can be rearranged to give the required result:

$$
\begin{aligned}
&\left\langle \eta' v' \Lambda'; S\Sigma' \middle| T_{\Omega'-\Omega}^k(\mu; J'\Omega' J\Omega) \middle| \eta v \Lambda; S\Sigma' \right\rangle \\
&= (-1)^{J'-\Omega'} \begin{pmatrix} J' & k & J \\ -\Omega' & \Omega'-\Omega & \Omega \end{pmatrix}^{-1} \sum_{N,N'} (-1)^{N'-N+\Omega'-\Omega+S+J+\Lambda'+k} (2N+1)(2N'+1) \begin{pmatrix} J' & S & N' \\ \Omega' & -\Sigma' & -\Lambda' \end{pmatrix} \begin{pmatrix} J & S & N \\ \Omega & -\Sigma & -\Lambda \end{pmatrix} \\
&\times \begin{Bmatrix} N' & J' & S \\ J & N & k \end{Bmatrix} \begin{pmatrix} N' & k & N \\ -\Lambda' & \Lambda'-\Lambda & \Lambda \end{pmatrix} \left\langle \eta' v' \Lambda' \middle| T_{\Lambda'-\Lambda}^k(\mu; N'N) \middle| \eta v \Lambda \right\rangle
\end{aligned} \tag{7}
$$

Relationship between Hund's case (a) and base (b) vibronic matrix elements when the vibronic matrix elements are independent of *N*

If we make the assumption that the vibronic matrix element, $\left\langle \eta' v' \Lambda' \middle| T_{\Lambda'-\Lambda}^k(\mu; N'N) \middle| \eta v \Lambda \right\rangle$, is independent of *N* then this can be taken out of the sum, and we are left with the following sum:

$$
\begin{aligned}
Z &= \sum_{N,N'} (-1)^{N'-N+\Omega'-\Omega+S+J+\Lambda'+k} (2N+1)(2N'+1) \begin{pmatrix} J' & S & N' \\ \Omega' & -\Sigma' & -\Lambda' \end{pmatrix} \begin{pmatrix} J & S & N \\ \Omega & -\Sigma & -\Lambda \end{pmatrix} \begin{Bmatrix} N' & J' & S \\ J & N & k \end{Bmatrix} \begin{pmatrix} N' & k & N \\ -\Lambda' & \Lambda'-\Lambda & \Lambda \end{pmatrix} \\
&= (-1)^{\Omega'-\Omega+S+J+\Lambda'+k} \sum_{N,N'} (-1)^{N'-N} (2N+1)(2N'+1) \begin{pmatrix} J' & S & N' \\ \Omega' & -\Sigma' & -\Lambda' \end{pmatrix} \begin{pmatrix} J & S & N \\ \Omega & -\Sigma & -\Lambda \end{pmatrix} \begin{Bmatrix} N' & J' & S \\ J & N & k \end{Bmatrix} \begin{pmatrix} N' & k & N \\ -\Lambda' & \Lambda'-\Lambda & \Lambda \end{pmatrix}
\end{aligned} \tag{8}
$$

which results in:

$$
\left\langle \eta' v' \Lambda'; S\Sigma' \middle| T_{\Omega'-\Omega}^k(\mu; J'\Omega' J\Omega) \middle| \eta v \Lambda; S\Sigma \right\rangle = (-1)^{J'-\Omega'} \begin{pmatrix} J' & k & J \\ -\Omega' & \Omega'-\Omega & \Omega \end{pmatrix}^{-1} Z \left\langle \eta' v' \Lambda' \middle| T_{\Lambda'-\Lambda}^k(\mu; N'N) \middle| \eta v \Lambda \right\rangle \tag{9}
$$

The value of this sum is actually a known identity if Σ = Σ'; Brink and Satchler (1968) give the following (Apendix II, p141):

$$\sum_{cf}(2c+1)(2f+1)(-1)^{a+b+c+d}(-1)^{f-e-\alpha-\delta}\begin{Bmatrix} a & b & e \\ d & c & f \end{Bmatrix}\begin{pmatrix} c & a & f \\ \gamma & \alpha & \phi \end{pmatrix}\begin{pmatrix} b & d & f \\ \beta & \delta & -\phi \end{pmatrix}\begin{pmatrix} d & c & e \\ \delta & \gamma & \varepsilon \end{pmatrix} = \begin{pmatrix} a & b & e \\ \alpha & \beta & -\varepsilon \end{pmatrix} \tag{10}$$

Making the identifications $c = N'$, $f = N$, $a = k$, $d = S$, $b = J$, $e = J'$, $\alpha = \Lambda - \Lambda'$, $\beta = \Omega$, $\gamma = -\Lambda'$, $\delta = -\Sigma$, $\varepsilon = \Omega'$ and $\phi = \Lambda$, gives (after some rearranging):

$$(-1)^{J+S+J'+\Lambda'-\Omega+k}\sum_{N'N}(-1)^{N'-N}(2N'+1)(2N+1)\begin{pmatrix} J' & S & N' \\ \Omega' & -\Sigma & -\Lambda' \end{pmatrix}\begin{pmatrix} J & S & N \\ \Omega & -\Sigma & -\Lambda \end{pmatrix}\begin{Bmatrix} N' & J' & S \\ J & N & k \end{Bmatrix}\begin{pmatrix} N' & k & N \\ -\Lambda' & \Lambda'-\Lambda & \Lambda \end{pmatrix} = \begin{pmatrix} J' & k & J \\ -\Omega' & \Lambda'-\Lambda & \Omega \end{pmatrix} \tag{11}$$

Substituting this back into the expression for the sum gives:

$$Z = (-1)^{J'-\Omega'}\begin{pmatrix} J' & k & J \\ -\Omega' & \Lambda'-\Lambda & \Omega \end{pmatrix} \tag{12}$$

provided Σ = Σ'. Substituting back into the relationship between the transition moments we have the expected relationship were Σ = Σ':

$$\langle \eta' v' \Lambda' | T^k_{\Lambda'-\Lambda}(\mu; J'\Omega' J\Omega) | \eta v \Lambda \rangle = \langle \eta' v' \Lambda' | T^k_{\Lambda'-\Lambda}(\mu; N' N) | \eta v \Lambda \rangle \tag{13}$$

Given this is describing a transformation between orthogonal basis sets, the sum *Z* will be zero if Σ' ≠ Σ. This has been checked by numerical evaluation of the sum, *Z*, for a range of *J* values up to 20.

References

D.M. Brink and G.R. Satchler, “Angular Momentum”, 2nd Ed, OUP, 1968.

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J.S.A. Brooke, R.S. Ram, C.M. Western, D.W. Schwenke, G. Li and P.F. Bernath, Einstein A coecients and oscillator strengths for the $A^2\Pi$-$X^2\Sigma^+$ (red) and $B^2\Sigma^+$-$X^2\Sigma^+$ (violet) systems and rovibrational transitions in the $X^2\Sigma^+$ state of CN. Astrophys. J. Supp Ser **210**, 23 (2014).