A Note on the Evaluation of Nuclear Quadrupole HFS Multiplet Patterns of Molecular Rotational Transitions

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The intensity weighted mean over the nuclear quadrupole hyperfine structure multiplet of a molecular rotational transition yields, to first order, the "undisturbed" rotational transition frequency. This fact may serve to effectively separate the two interrelated problems of calculating the rotational constants of the molecule from the "undisturbed" frequencies and the nuclear quadrupole coupling parameters from the multiplet splitting patterns.

The majority of molecules have no electronic angular momentum. If any hyperfine structure of rotational levels is observed, it is therefore prominently [1] due to the interaction between a nuclear quadrupole moment and the gradient of the electrical field produced at this nuclear position by the remaining molecular charges. This interaction causes the respective nuclear spin $\boldsymbol{I}$ and the molecular rotation $\boldsymbol{J}$ to couple to a resultant $\boldsymbol{F}$. An evaluation of the rotational spectrum in the microwave region including the hfs then yields besides the rotational constants of the molecule the nuclear quadrupole coupling parameters.

It is the purpose of this paper to call the attention to a property of the interaction energy which holds in first order and facilitates the task of finding correct rotational constants from a rotational spectrum split by hfs, yet does not appear to have been utilized before in this branch of spectroscopy.

1st Order Interaction Energy

Let $H = H_r + H_Q$ be the total Hamiltonian of the rotating molecule including an interaction H_Q of the above considered type. We shall assume in this paper that only a single quadrupolar nucleus exists. H_r is the rotational energy operator of a rigid asymmetric top [2]

$$H_r = A J_a^2 + B J_b^2 + C J_c^2 \qquad (1)$$

(a, b, c principal axes of inertia; A, B, C rotational constants; J_g components of angular momentum $\boldsymbol{J}$). Let the interaction be represented by the scalar product

$$H_Q = \mathbf{V}^{(k)} \cdot \mathbf{Q}^{(k)} \qquad (2)$$

of two commuting irreducible tensor operators [3] of rank k. The space on which $\mathbf{V}$ operates is characterized by the eigenstates of the complete set of commuting observables $\boldsymbol{J}^2$, the space-fixed component J_Z of $\boldsymbol{J}$, and the rigid-rotor energy H_r, whereas $\mathbf{Q}$ operates on the space pertaining to the observables $\boldsymbol{I}^2$ and I_Z. In the coupled representation in which $\boldsymbol{J}^2$, H_r, $\boldsymbol{I}^2$ as well as $\boldsymbol{F}^2 = (\boldsymbol{J}+\boldsymbol{I})^2$ and F_Z are diagonal with the eigenvalues $J(J+1)$, $W_r = \frac{1}{2}(A+C) \cdot J(J+1) + \frac{1}{2}(A-C) E_{J\tau}(\varkappa)$, $I(I+1)$, $F(F+1)$, M_F respectively [4], we have

$$(J\,\tau\,I\,F\,M_F \,|\, H \,|\, J\,\tau\,I\,F\,M_F) = W_r + W_Q \qquad (3)$$

where the first-order perturbation energy has been shown [5] to be

$$\begin{aligned} W_Q &= (J\,\tau\,I\,F\,M_F \,|\, \mathbf{V}^{(k)} \cdot \mathbf{Q}^{(k)} \,|\, J\,\tau\,I\,F\,M_F) \\ &= (-1)^{F+J+I} \begin{Bmatrix} F & J & I \\ k & I & J \end{Bmatrix} (J\,\tau \,\|\, \mathbf{V}^{(k)} \,\|\, J\,\tau) \\ &\quad \cdot (I \,\|\, \mathbf{Q}^{(k)} \,\|\, I). \end{aligned} \qquad (4)$$

The curly bracket is a Wigner 6-j symbol, followed by the reduced matrix elements of the tensors $\mathbf{V}^{(k)}$ and $\mathbf{Q}^{(k)}$. In the specific case of nuclear quadrupole coupling to molecular rotation k is two and [6]

$$\begin{Bmatrix} F & J & I \\ 2 & I & J \end{Bmatrix} = 2(-1)^{F+J+I} \frac{\frac{3}{4} C(C+1) - I(I+1)\, J(J+1)}{\sqrt{(2I-1)\, I(2I+1)\, (I+1)\, (2I+3)\, (2J-1)\, J(2J+1)\, (J+1)\, (2J+3)}} \qquad (5)$$

[1] Magnetic spin-rotation or spin-spin coupling effects have been observed only in exceptional cases.

[2] G. W. KING, R. M. HAINER, and P. C. CROSS, J. Chem. Phys. **11**, 27 [1943].

[3] A. R. EDMONDS, Drehimpulse in der Quantenmechanik, Bibliographisches Institut, Mannheim 1964, chapter 7.2. There $\mathbf{V}^{(k)}$ and $\mathbf{Q}^{(k)}$ for nuclear quadrupole coupling are defined in terms of spherical harmonics.

[4] $\varkappa = (2B-A-C)/(A-C)$ asymmetry parameter; $E_{J\tau}(\varkappa)$ "reduced" energy of the rigid rotor, see [2].

[5] Ref. [3], Eq. 7.1.6.

[6] E. g. ref. [3], appendix Table 5.

where $C \equiv F(F+1) - J(J+1) - I(I+1)$.

The reduced matrix element of the nuclear quadrupole moment tensor $\mathbf{Q}^{(2)}$ may be evaluated by means of the Wigner-Eckart theorem to give [7]

$$(I \,\|\, \mathbf{Q}^{(2)} \,\|\, I) = \frac{(I\, M_I{=}I \,|\, Q_0^{(2)} \,|\, I\, M_I{=}I)}{\begin{pmatrix} I & 2 & I \\ -I & 0 & I \end{pmatrix}} = \frac{eQ}{2}\sqrt{\frac{(I+1)\,(2I+1)\,(2I+3)}{I(2I-1)}}. \tag{6}$$

$Q_0^{(2)}$ signifies the zero standard component of the tensor $\mathbf{Q}^{(2)}$, the large bracket denotes a Wigner 3-j symbol, the abbreviation Q is generally referred to as the "nuclear quadrupole moment [8]". Likewise we may obtain for the reduced matrix element of the field gradient tensor $\mathbf{V}^{(2)}$

$$(J\tau \,\|\, \mathbf{V}^{(2)} \,\|\, J\tau) = \frac{(J\tau\, M_J{=}J \,|\, V_0^{(2)} \,|\, J\tau\, M_J{=}J)}{\begin{pmatrix} J & 2 & J \\ -J & 0 & J \end{pmatrix}} = \frac{q_{J\tau}}{2}\sqrt{\frac{(J+1)\,(2J+1)\,(2J+3)}{J(2J-1)}}. \tag{7}$$

$q_{J\tau}$ is essentially the field gradient component along the direction of $\mathbf{J}$. For the general asymmetric top it may be expressed as [9]

$$q_{J\tau} = \frac{2}{(J+1)\,(2J+3)} \sum_{\substack{g \\ a,b,c}} \left(\frac{\partial^2 V}{\partial g^2}\right)_0 \langle J_g^2 \rangle_{J\tau} \tag{8}$$

where the $(\partial^2 V/\partial g^2)_0$ are the (constant) components of the electrical field gradient tensor taken along directions parallel to the principal axes of inertia at the nuclear position, and the $\langle J_g^2 \rangle_{J\tau}$ the expectation values of the squares of the angular momentum components depending on the specific rotational state $J\tau$ and on the inertial asymmetry parameter $\varkappa$ of the molecule [9]. With [10]

$$\chi_{gg} \equiv eQ\left(\frac{\partial^2 V}{\partial g^2}\right)_0 \tag{9}$$

we finally arrive at the familiar first-order interaction energy formula [11–15]

$$W_Q = \frac{2J+3}{J} f(I,J,F)\, eQ\, q_{J\tau} = \frac{2}{J(J+1)} f(I,J,F) \sum_{\substack{g \\ a,b,c}} \chi_{gg} \langle J_g^2 \rangle_{J\tau} \tag{10}$$

where $f(I,J,F)$ has been called Casimir's function (tabulated in ref. [12, 14])

$$f(I,J,F) \equiv \frac{\frac{1}{2}C(C+1) - I(I+1)\,J(J+1)}{2I(2I-1)\,(2J+3)\,(2J-1)}. \tag{11}$$

Relative Multiplet Line Strengths

Let $\mathbf{P}^{(l)}$ be an l-rank irreducible tensor operator of the system considered with the standard components $P_q^{(l)}$ which interacts with an external radiation field thereby producing transitions of the system. $\mathbf{P}^{(l)}$ shall operate on the same space as $\mathbf{V}^{(k)}$, here the space of the commuting observables $\mathbf{J}^2$, J_Z, H_r [eigenvalues $J(J+1)$, M_J, $W_r(J,\tau)$]. When this space is isolated the line strength of a transition $J\tau \to J'\tau'$ has been defined as [16, 17]

$$S(J\tau, J'\tau') = \sum_{M_J q M_J'} |(J\tau\, M_J \,|\, P_q^{(l)} \,|\, J'\tau'\, M_J')|^2 = |(J\tau \,\|\, \mathbf{P}^{(l)} \,\|\, J\tau)|^2. \tag{12}$$

In the coupled representation we have, however, for the individual component $F \to F'$ of the transition $J\tau \to J'\tau'$ (I does not change) the line strength [18]

$$S(J\tau IF, J'\tau' IF') = |(J\tau IF \,\|\, \mathbf{P}^{(l)} \,\|\, J'\tau' IF')|^2 = (2F+1)\,(2F'+1) \begin{Bmatrix} F & J & I \\ J' & F' & l \end{Bmatrix}^2 |(J\tau \,\|\, \mathbf{P}^{(l)} \,\|\, J'\tau')|^2 = (2F+1)\,(2F'+1) \begin{Bmatrix} F & J & I \\ J' & F' & l \end{Bmatrix}^2 S(J\tau, J'\tau'). \tag{13}$$

Summing over the final states F' we obtain by the orthogonality property of the 6-j symbols [19]

$$\sum_{\substack{F'= \\ F, F\pm 1}} S(J\tau IF, J'\tau' IF') = \frac{2F+1}{2J+1} S(J\tau, J'\tau'). \tag{14}$$

[7] Ref. [3], Eq. 5.4.1. and chapter 7.2.

[8] This definition agrees with that of N. F. Ramsey, Nuclear Moments, J. Wiley and Sons, New York and London 1953, Sect. 2 A, Eq. (9). See also footnote, this ref., p. 5.

[9] J. K. Bragg and S. Golden, Phys. Rev. **75**, 735 [1949], Eq. (1).

[10] Laplace's equation shows that there are only two independent nuclear quadrupole coupling parameters (for the asymmetric top) $\sum_g \chi_{gg} = 0$.

[11] H. B. G. Casimir, On the Interaction between Atomic Nuclei and Electrons, W. H. Freeman and Company, San Francisco and London 1963.

[12] W. Gordy, W. V. Smith, and R. F. Trambarulo, Microwave Spectroscopy, Chapman and Hall, London 1953, Chapter 2.6.

[13] M. W. P. Strandberg, Microwave Spectroscopy, Methuen, London 1954, Chapter IV.

[14] C. H. Townes and A. L. Schawlow, Microwave Spectroscopy, McGraw-Hill Ltd., London 1955, Chapters 5.7 and 6.

[15] T. M. Sugden and C. N. Kenney, Microwave Spectroscopy of Gases, D. van Nostrand Ltd., London 1965, Chapter 6.

[16] Ref. [3], Eq. 5.4.7.

[17] E. U. Condon and G. H. Shortley, The Theory of Atomic Spectra, University Press, Cambridge 1957, p. 98.

[18] Ref. [3], Eq. 7.1.7, see also ref. [17], p. 238.

[19] Ref. [3], Eq. 6.2.9.

This equation contains the Ornstein-Burger-Dorgelo sum rule [20]. Summing further over the initial states F from $|J-I|$ to $J+I$ one obtains the total line strength in the multiplet

$$\sum_F \sum_{F'} S(J\tau I F, J'\tau' I F') = (2I+1)\, S(J\tau, J'\tau') \tag{15}$$

a result to be expected in view of the $2I+1$ multiplicity of each level $J\tau$ in the limit of vanishing coupling in the combined spaces of $\mathbf{V}^{(k)}$ and $\mathbf{Q}^{(k)}$. The relative line strength of a multiplet component is therefore

$$s(J I F, J' I F') \equiv \frac{S(J\tau I F, J'\tau' I F')}{\sum_{FF'} S(J\tau I F, J'\tau' I F')} = \frac{(2F+1)(2F'+1)}{2I+1} \begin{Bmatrix} F & J & I \\ J' & F' & l \end{Bmatrix}^2 . \tag{16}$$

It is obviously independent of τ and τ'. In our particular case $\boldsymbol{P}^{(l)}$ is the permanent electrical dipole moment tensor of the molecule, and l equals one (vector). The components of this tensor may be chosen as

$$\begin{aligned} P^{(1)}_{\pm 1} &= \mp \frac{1}{\sqrt{2}} (P_X \pm i P_Y) \\ &= \mp \frac{1}{\sqrt{2}} \sum_g \mu_g (\Phi_{Xg} \pm i \Phi_{Yg}) = \sum_g \mu_g \Phi^{(1)}_{\pm 1, g} \\ P^{(1)}_0 &= P_Z = \sum_g \mu_g \Phi_{Zg} = \sum_g \mu_g \Phi^{(1)}_{0,g} \end{aligned} \tag{17}$$

where the Φ_{Gg} $(G = X, Y, Z;\ g = a, b, c)$ denote the direction cosine operators between the space-fixed (G) and the body-fixed (g) reference frames. They form for each g a first-rank irreducible tensor operator $\boldsymbol{\Phi}_g{}^{(1)}$. The μ_g are the (constant) components of the dipole moment resolved along the body-fixed directions g. Since, as a consequence of the selection rules, any particular rotational transition $J\tau \rightarrow J'\tau'$ is produced by only one component μ_g it is customary to take as the line strength of a rotational transition the quantity [21]

$$\begin{aligned} S^g(J\tau, J'\tau') &= \sum_{M_J q M_{J'}} |(J\tau M_J | \Phi^{(1)}_{q,g} | J'\tau' M_J')|^2 \\ &= |(J\tau \| \boldsymbol{\Phi}^{(1)}_g \| J\tau)|^2 \end{aligned} \tag{18}$$

rather than (12) and denote g explicitly. The expression for the relative multiplet line strength in the coupled representation does not change, we obtain in our case Eq. (16) with $l=1$ for the relative line strength of the individual component $F \rightarrow F'$ of the nuclear quadrupole hfs multiplet for a rotational transition $J \rightarrow J'$. This quantity is independent also of g and has been tabulated [14].

Intensity Weighted Mean over a hfs Multiplet

The energy is to first order (in frequency units), Eq. (3),

$$W(J\tau I F) = W_r(J\tau) + W_Q(J\tau I F)$$

and the transition frequency of an individual hfs component is given by

$$\begin{aligned} \nu(J\tau I F, J'\tau' I F') &= \nu_r(J\tau, J'\tau') \\ &\quad + W_Q(J'\tau' I F') - W_Q(J\tau I F) \end{aligned} \tag{19}$$

where ν_r is the transition frequency if no hfs were present. Weighting each hfs component by its relative line strength s and summing over all components of a multiplet one obtains, since $\sum_{FF'} s = 1$,

$$\begin{aligned} &\sum_{FF'} \nu(J\tau I F, J'\tau' I F') \cdot s(J I F, J' I F') \\ &= \nu_r(J\tau, J'\tau') + \sum_{FF'} W_Q(J'\tau' I F') \cdot s(J I F, J' I F') \\ &\quad - \sum_{FF'} W_Q(J\tau I F) \cdot s(J I F, J' I F') . \end{aligned} \tag{20}$$

Both sums of the right hand member of the equation may be shown to vanish. We have from (4) and (16), leaving k and l yet unspecified,

$$\begin{aligned} &\sum_{FF'} W_Q(J\tau I F) \cdot s(J I F, J' I F') \\ &= \frac{(J\tau \| \mathbf{V}^{(k)} \| J\tau)\,(I \| \mathbf{Q}^{(k)} \| I)}{2I+1} \\ &\quad \times \sum_F (-1)^{F+J+I} \begin{Bmatrix} F & J & I \\ k & I & J \end{Bmatrix} (2F+1) \\ &\quad \times \sum_{F'} (2F'+1) \begin{Bmatrix} F & J & I \\ J' & F' & l \end{Bmatrix}^2 . \end{aligned} \tag{21}$$

The sum over F' yields $(2J+1)^{-1}$ which is independent of F and has been used before, (14). The sum over F may be evaluated utilizing the orthogonality property of the 6-j symbols [22] to give $\delta_{k0} \sqrt{(2I+1)(2J+1)}$ which vanishes since in our

[20] Ref. [17], p. 238.

[21] R. H. Schwendeman and V. W. Laurie, Tables of Line Strengths for Rotational Transitions of Asymmetric Rotor Molecules, Pergamon Press, London 1958.

[22] A. Messiah, Quantum Mechanics, Vol. II, North Holland Publishing Company, Amsterdam 1965, p. 1065, Eq. C. 35.b. This equation may be derived from the orthogonality C. 35.c. using C. 37.

case k equals two [23]. Interchanging $J\,\tau\,F$ and $J'\,\tau'\,F'$ to obtain the remaining sum one arrives at the corresponding result. We therefore have the following simple statement

$$\sum_{FF'} \nu(J\,\tau\,I\,F, J'\,\tau'\,I\,F') \cdot s(J\,I\,F, J'\,I\,F') = \nu_r(J\,\tau, J'\,\tau') \,. \tag{22}$$

The line strength weighted mean over the multiplet frequencies yields, to first order, the „undisturbed" frequency of the particular transition. This statement is indeed a familiar one in other branches of spectroscopy. It is a consequence of the fact that the first-order perturbation energies of an operator of type (2) when multiplied by the respective space degeneracy factors $2F+1$, in (22) supplied by the existence of the sum rule (14), add up to zero. The result does not depend on k as long as this is nonvanishing nor on l. It applies for example to the spin-orbit coupling (LS) of atomic spectroscopy. We could, however, find no record of Eq. (22) having been previously used in rotational spectroscopy to effectively separate the two problems of calculating the rotational constants of the molecule as well as the quadrupole coupling parameters from a spectrum.

The "undisturbed" rotational transition frequencies are the ones that must be included in a least-squares determination of the rotational constants. Computer programs written for the analysis of a rotational spectrum complicated by nuclear quadrupole hfs make use of iterative procedures because, in order to calculate the χ_{gg} from the hfs splitting patterns, the $\langle J_g^2 \rangle_{J\tau}$ must be known which depend on the rotational constants A, B, C through the asymmetry parameter $\varkappa$. $\varkappa$, in turn, must be derived from the "undisturbed" frequencies which, without the help of (22), can be established only *after* the analysis of the hfs patterns has been completed. However, using Eq. (22) first-order accurate "undisturbed frequencies" and hence rotational constants can be determined without any prior analysis of the nuclear quadrupole hfs. An assignment $F \rightarrow F'$ of the individual components of a measured multiplet *need not* be made. Also partially resolved or coinciding components are properly accounted for by simply choosing the intensity weighted mean or "center of gravity" of the multiplet. The errors introduced by the fact that the intensity (in the microwave region) is proportional to the product of line strength times frequency squared rather than to line strength itself should be negligible since in most cases the hfs splitting is very small compared with the frequency. The fact that first-order theory is not adequate to treat wide hfs splittings (J is then no longer a good quantum number [24]), further the intermingling of hfs components with vibrational satellites or hfs components of different rotational transitions, may more often limit the applicability of the simple procedure proposed here though even then it may occasionally be useful as a first approach.

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[23] Eq. (21) for $k=2$ is proportional to the sum

$$\sum_{FF'} f(I, J, F) \cdot s(J\,I\,F, J'\,I\,F').$$

Since both f and s have been tabulated, it may also be verified numerically that the sum (21) vanishes.

[24] It has been vital for the above proof that states with different J do not mix.