

On the Theory of Vibronic Interactions

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A detailed derivation of the general expressions needed for the evaluation of the intensities of vibronically induced transitions is presented.

From the theoretical point of view, electronic transitions between orbitals of similar parity and localized on the central ion of the transition metal complexes are strictly LAPORTE-forbidden¹. Such transitions, nonetheless, *do occur* and are responsible for the colors of the ions of the transition metals. A way out of this contradiction was first proposed by VAN VLECK² who suggested that the transitions in the "centric" complex molecules were due to the perturbation caused by a quantum of ungerade vibration which made the transitions *vibronically* allowed. In the present paper, we develop a general formulation expressing these vibronic interactions. Although the theory of vibronically induced transitions has been discussed by several investigators in the past³⁻⁶, to our knowledge, the development presented here, along with Appendix A, is probably the most complete account given about the subject.

1. Theory

The theoretical oscillator strength for a transition is given by

$$f_{k \rightarrow k'} = \frac{4\pi m c}{3\hbar e^2} \nu_{kk'} G_{kk'} |\mathbf{M}_{kk'}|^2 = \beta \nu_{kk'} G_{kk'} P_{kk'} \quad (1)$$

where all the symbols except $\nu_{kk'}$, $G_{kk'}$, $\mathbf{M}_{kk'}$ and $P_{kk'}$ have their usual meaning. $\nu_{kk'}$ stands for the frequency of transition in KAYSERS, $G_{kk'}$ the degeneracy of the upper level, $\mathbf{M}_{kk'}$ the transition moment, and $P_{kk'}$ the transition probability for an electric dipole transition. $\mathbf{M}_{kk'}$ is given by

$$\mathbf{M}_{kk'} = -e \langle \Psi_k(x, Q) | \sum_i^{\text{electrons}} \mathbf{r}_i | \Psi_{k'}(x, Q) \rangle \quad (2)$$

* Supported by the Dean's Fund for Research at Northern Illinois University.

¹ O. LAPORTE, Phys. Rev. **61**, 302 [1942].

² J. H. VAN VLECK, J. Chem. Phys. **41**, 67 [1937].

³ A. LIEHR and C. J. BALLHAUSEN, Phys. Rev. **106**, 1161 [1957].

⁴ A. C. ALBRECHT, J. Chem. Phys. **33**, 156 [1960].

where x represents the collection of electronic coordinates, and Q the collection of nuclear coordinates. In what follows, we shall, for simplicity, consider only the oscillator strength of that part of the transition which is polarized in the x direction, bearing in mind that similar expressions hold for polarizations in the z and y directions.

The total wave function for a vibronic state is written in the BORN-OPPENHEIMER form

$$|\Psi_{kl}(x, Q)\rangle = |\Theta_k(x, Q)\rangle |\Phi_l^k(Q)\rangle \quad (3)$$

where $|\Theta_k(x, Q)\rangle$ is a solution of the electronic SCHRÖDINGER equation

$$H_{\text{el.}}(x, Q) |\Theta_k(x, Q)\rangle = \left\{ -\frac{\hbar^2}{2m} \sum_i \nabla_i^2 + U_{\text{el.}}(x, Q) \right\} |\Theta_k(x, Q)\rangle = E_{\text{el.}}^k |\Theta_k(x, Q)\rangle \quad (4a)$$

and $|\Phi_l^k(Q)\rangle$ is a vibrational wave function l belonging to the electronic state k , and satisfying

$$H_{\text{vibr.}} |\Phi_l^k(Q)\rangle = \left\{ -\frac{\hbar^2}{2} \sum_a \frac{\partial^2}{\partial Q_a^2} + U_{\text{vibr.}}(Q) \right\} |\Phi_l^k(Q)\rangle = E_{\text{vibr.}}^{kl} |\Phi_l^k(Q)\rangle \quad (4b)$$

For a transition from a vibrational level l of the k -th electronic state to the l' level of the k' -th state, the transition probability is given by

$$P_{kk'}^{ll'} = |\langle \Psi_{kl}(x, Q) | m(x) | \Psi_{k'l'}(x, Q) \rangle|^2 \quad (5a)$$

$$= |\langle \Phi_l^k(Q) | M_{kk'}(Q) | \Phi_{l'}^{k'}(Q) \rangle|^2 \quad (5b)$$

where $M_{kk'}(Q)$ is the transition moment given by

$$M_{kk'}(Q) = \langle \Theta_k(x, Q) | m(x) | \Theta_{k'}(x, Q) \rangle \quad (5c)$$

The transition probability from l of k to all levels l' of k' is given⁷ by

⁵ J. A. POPE and J. W. SIDMAN, J. Chem. Phys. **27**, 1270 [1957].

⁶ J. N. MURRELL and J. A. POPE, Proc. Phys. Soc. London A **69**, 249 [1956].

⁷ The sums which are not specified in what follows contain a $(3N-6)$ fold infinity of terms (nonlinear molecules of N atoms).



$$P_{kk'}^l = \sum P_{kk'}^l = \sum |M_{kk'}^{ll'}|^2, \quad (6a)$$

$$P_{kk'}^l = \sum |\langle \Phi_l^k(Q) | M_{kk'}^2(Q) | \Phi_l^{k'}(Q) \rangle|^2 \quad (6b)$$

which by the quantum mechanical sum rule⁸ gives

$$P_{kk'}^l = \langle \Phi_l^k(Q) | M_{kk'}^2(Q) | \Phi_l^k(Q) \rangle = \langle M_{kk'}^2(Q) \rangle_l. \quad (6c)$$

Finally, the *total transition probability* is

$$P_{kk'} = |M_{kk'}|^2 = \sum_l B_l \langle M_{kk'}^2(Q) \rangle_l \quad (7)$$

where B_l is the BOLTZMANN population of the l -th vibrational level of the k -th electronic state.

Now expanding $M_{kk'}^2(Q)$ in TAYLOR Series about $Q=0$, we have

$$M_{kk'}^2(Q) = M_{kk'}^2(0) + \sum_a \left(\frac{\partial M_{kk'}^2}{\partial Q_a} \right) \cdot Q_a + \frac{1}{2!} \sum_a \sum_b \left(\frac{\partial^2 M_{kk'}^2}{\partial Q_a \partial Q_b} \right)_0 \cdot Q_a Q_b + \dots \quad (8a)$$

where Q_a is the a -th normal coordinate. Further algebraic simplification gives

$$M_{kk'}^2(Q) = M_{kk'}^2(0) + 2 M_{kk'}(0) \sum_a \left(\frac{\partial M_{kk'}}{\partial Q_a} \right)_0 \cdot Q_a + \sum_a \sum_b \left(\frac{\partial M_{kk'}}{\partial Q_a} \right)_0 \cdot \left(\frac{\partial M_{kk'}}{\partial Q_b} \right)_0 \cdot Q_a Q_b + \dots \quad (8b)$$

Substituting Eq. (8b) in Eq. (7) and neglecting nonlinear terms, we have

$$P_{kk'} \cong \sum_l B_l \langle M_{kk'}^2(0) \rangle_l + 2 \sum_l B_l M_{kk'}(0) \sum_a \left(\frac{\partial M_{kk'}}{\partial Q_a} \right)_0 \langle Q_a \rangle_l + \sum_a \sum_l \left(\frac{\partial M_{kk'}}{\partial Q_a} \right)_0^2 \cdot \langle Q_a^2 \rangle_l \cdot B_l \quad (9)$$

and since the second term, $\langle Q_a \rangle_l$, vanishes for harmonic oscillators, and since

$$\sum_l B_l = 1 \quad \text{and} \quad \langle M_{kk'}^2(0) \rangle_l \equiv M_{kk'}^2(0),$$

Eq. (9) reduces to

$$P_{kk'} \cong M_{kk'}^2(0) + \sum_a \left(\sum_l B_l \langle Q_a^2 \rangle_l \right) \cdot \left(\frac{\partial M_{kk'}}{\partial Q_a} \right)_0^2 \quad (10a)$$

which, as Appendix A shows, gives the following temperature dependent relationship

$$P_{kk'} \cong M_{kk'}^2(0) + \sum_a \frac{h}{8 \pi^2 \nu_a} \text{ctnh} \left(\frac{h \nu_a}{2 k T} \right) \cdot \left(\frac{\partial M_{kk'}}{\partial Q_a} \right)_0^2. \quad (10b)$$

Finally, within the framework of the HERZBERG-TELLER theory⁹ we treat the nuclear motions as perturbations in the electronic SCHRÖDINGER equation, such that

$$H_{el.} = \left\{ -\frac{\hbar^2}{2m} \sum_i \nabla_i^2 + U(x, 0) \right\} + H'_{vibronic}(Q). \quad (11)$$

Thus, using the zeroth order wave functions valid for the equilibrium nuclear positions of the unperturbed electronic states, we have

$$| \Theta_k(x, Q) \rangle = | \Theta_k(x, 0) \rangle + \sum_{s \neq k} \lambda_{ks}(Q) | \Theta_s(x, 0) \rangle \quad (12a)$$

where if $H'(Q)$ is the first order perturbation caused by the electronic state s , $\lambda_{ks}(Q)$ is given by

$$\lambda_{ks}(Q) = - \langle \Theta_k^0 | H'(Q) | \Theta_s^0 \rangle / (E_k^0 - E_s^0) \quad (12b)$$

where $| \Theta_k^0 \rangle \equiv | \Theta_k(x, 0) \rangle$.

Substituting Eq. (12a) in Eq. (5c) and neglecting nonlinear terms we obtain

$$M_{kk'}(Q) \cong M_{kk'}(0) + \sum_{s \neq k} \lambda_{ks} M_{sk'}(0) + \sum_{s \neq k'} \lambda_{k's} M_{ks}(0) \quad (13)$$

which when differentiated with respect to Q_a and evaluated at $Q_a=0$ gives

$$\left(\frac{\partial M_{kk'}}{\partial Q_a} \right)_0 \cong \sum_{s \neq k} \left(\frac{\partial \lambda_{ks}}{\partial Q_a} \right)_0 M_{sk'}(0) + \sum_{s \neq k'} \left(\frac{\partial \lambda_{k's}}{\partial Q_a} \right)_0 M_{ks}(0). \quad (14)$$

Finally, when Eq. (14) is substituted in Eq. (10b) and the result of this in Eq. (1), we have

$$f_{k \rightarrow k'} = 1.085 \times 10^{11} \nu_{kk'} G_{kk'} \left[M_{kk'}^2(0) + \sum_a \frac{h}{8 \pi^2 \nu_a} \text{ctnh} \left(\frac{h \nu_a}{2 k T} \right) \left\{ \sum_{s \neq k} \left(\frac{\partial \lambda_{ks}}{\partial Q_a} \right)_0 M_{sk'}(0) + \sum_{s \neq k'} \left(\frac{\partial \lambda_{k's}}{\partial Q_a} \right)_0 M_{ks}(0) \right\}^2 \right] \quad (15a)$$

⁸ D. BOHM, Quantum Mechanics, Prentice-Hall, New York 1951.

⁹ G. HERZBERG and E. TELLER, Z. physik. Chem. B **21**, 410 [1933].

where

$$\left(\frac{\partial \lambda_{ks}}{\partial Q_a}\right)_0 = - \langle \Theta_k^0 | \left(\frac{\partial H'}{\partial Q_a}\right) | \Theta_s^0 \rangle / (E_k^0 - E_s^0) \quad (15b)$$

is the vibronic perturbation¹⁰ energy per unit displacement in the normal coordinate Q_a , resulting from the coupling of the electronic states k and s .

Our long journey through the preceding algebraic labyrinth culminated in the derivation of Eq. (15a); where when only $M_{kk'}^2(0)$ is nonvanishing, one speaks of *symmetry allowed* transitions and when only $(\partial M_{kk'}/\partial Q_a)_0$ is nonvanishing, one speaks of *vibronically induced* transitions. The existence of one does not exclude the existence of the other; for even in *parity allowed* transitions, one finds an enhancement of the said transitions by symmetric vibrations⁶.

Furthermore, the evaluation of the oscillator strength is simplified when group theoretical considerations are taken into consideration. It is noted that $M_{kk'}(0)$ is nonvanishing only if the direct product of the reps to which $|\Theta_k^0\rangle$, $|\Theta_{k'}^0\rangle$, and x belong (in the point group to which the molecule belongs) includes at least once the totally symmetric rep $\Gamma_1 (\equiv A_1)$. On the other hand, $(\partial M_{kk'}/\partial Q_a)_0$ is nonvanishing only when the direct product of the reps to which $|\Theta_k^0\rangle$, $|\Theta_{k'}^0\rangle$, x and ν_a belong to in the point group under discussion, includes at least once the totally symmetric rep Γ_1 . This procedure, alas, doesn't evaluate the integrals. They must be evaluated if one is to engage in quantitative rather than qualitative discussions.

Finally, we deem it wise to restate some of the assumptions upon which the theory was based, and let experiment be the critical judge of the validity of our approximations.

- (i) We have assumed that the BORN-OPPENHEIMER approximation is valid.
- (ii) We have assumed that the vibrational wave functions are the harmonic oscillator functions and have tacitly neglected anharmonicity.
- (iii) We have, furthermore, assumed that the bond distances and the force constants are the same in the combining electronic states, and the vibrational eigenfunctions in the two states are orthonormal or very nearly so, so that we could apply the quantum mechanical sum rule.

¹⁰ The reader, from a comparison of Eq.(4a) and Eq.(11), will notice that the perturbation HAMILTONIAN $U_{\text{vibronic}}(x, Q)$ is a potential energy operator.

- (iv) We have assumed that in the absence of spin-orbit coupling and/or hyperfine perturbation, there is no change of multiplicity.
- (v) Finally, we have assumed that, for our purposes, only first order vibronic interactions are important, and have neglected higher order interactions.

2. Some Computational Aspects

Evaluation of $(\partial H'/\partial Q_a)_0$

The quantity $(\partial H'/\partial Q_a)_0$ of Eq. (15b) may be written as

$$\left(\frac{\partial H'}{\partial Q_a}\right)_0 = \sum_i^{\text{el.}} \sum_\sigma^{\text{nucl.}} \left(\frac{\partial H'_{i\sigma}}{\partial Q_a}\right)_0 \quad (16a)$$

$$= \sum_i^e \sum_\sigma^N \left(\frac{\partial H'_{i\sigma}}{\partial r_{i\sigma}}\right)_0 \left(\frac{\partial r_{i\sigma}}{\partial Q_a}\right)_0 \frac{\mathbf{r}_{i\sigma}}{r_{i\sigma}} \quad (16b)$$

which, when one uses local cartesian coordinates ξ_σ^1 , ξ_σ^2 , and ξ_σ^3 localized on the nucleus σ , transforms Eq. (16b) into

$$\left(\frac{\partial H'}{\partial Q_a}\right)_0 = \sum_{i=1}^3 \sum_i^e \sum_\sigma^N \left(\frac{\partial H'_{i\sigma}}{\partial r_{i\sigma}}\right)_0 \left(\frac{\partial r_{i\sigma}}{\partial \xi_\sigma^i}\right)_0 \left(\frac{\partial \xi_\sigma^i}{\partial Q_a}\right)_0 \quad (16c)$$

where $(\partial r_{i\sigma}/\partial \xi_\sigma^i)_0$ is the direction cosine of the vector $\mathbf{r}_{i\sigma}$,

$$(\partial H'_{i\sigma}/\partial r_{i\sigma})_0 = +Z_\sigma e^2/r_{i\sigma}^2,$$

and $(\partial \xi_\sigma^i/\partial Q_a)_0$ are determined by a complete vibrational analysis of the molecule at hand, and are in fact the matrix elements of $[M^{-1}B'(L^{-1})']$ in

$$\xi = [M^{-1}B'(L^{-1})']Q \quad (17)$$

where B' is the transpose of the matrix B which transforms from the Cartesian displacement coordinates ξ to the symmetry coordinates S ,

$$S = B\xi \quad (18)$$

and $(L^{-1})'$ is the transpose of the matrix L^{-1} which transforms from the symmetry coordinates S to the normal coordinates Q ,

$$Q = L^{-1}S \quad (19)$$

and where M^{-1} is a diagonal matrix whose elements are the reciprocal masses of the appropriate nuclei.

Evaluation of the B Matrix

As mentioned earlier, the matrix B transforms from the Cartesian displacement coordinates δx_1 , δy_1 , δz_1 , δx_2 , δy_2 , δz_2 , ..., δx_{3N} , δy_{3N} , δz_{3N} to the symmetry coordinates $S_1, S_2, \dots, S_{3N-6}$.

At present, the most convenient method of setting up the symmetry coordinates is the application of the projection operator

$$P_{\lambda k}^{(j)} = \frac{l j}{h} \sum \Gamma^{(j)}(R)_{\lambda k} \cdot R$$

on an appropriate set of internal coordinates such as bond stretches and angle-bends¹¹. Thus the column vector R , whose components are the internal coordinates, is linearly transformed into the column vector S , such that

$$S = A R. \quad (20)$$

Furthermore, the internal coordinates themselves can be expressed in terms of the $3N$ Cartesian coordinates localized on the nuclei of the molecule in question, such that

$$R = C \xi, \quad (21)$$

and therefore

$$S = [A C] \xi = B \xi. \quad (22)$$

The A matrices of almost all types of molecules can be found dispersed in the literature. The C matrix elements, on the other hand, can be determined, in most molecules of interest, by the following relations:

- (i) The bond-stretch δr_{ij} between nuclei i and j (see Fig. 1) is given by

$$\delta r_{ij} = -\delta y_i - \delta z_j, \quad (23)$$

- (ii) For an angle α_{ikj} whose equilibrium value is 90° , the angle-bend $\delta \alpha_{ikj}$ (see Fig. 2) is given by

$$\delta \alpha_{ikj} = r_{kj}^{-1} [\delta z_k - \delta x_j] + r_{ki} [\delta y_k - \delta y_i] \quad \text{and} \quad (24)$$

- (iii) For an angle α_{ikj} whose equilibrium value is 180° , the angle-bend $\delta \alpha_{ikj}$ (see Fig. 3) is given by

$$\delta \alpha_{ikj} = r^{-1} [\delta y_i - \delta x_j + 2 \delta z_k] \quad (25)$$

where we assume $r_{ik} = r_{kj} \equiv r$.

Finally, it should be brought to the reader's attention that the mathematical formalism to calculate

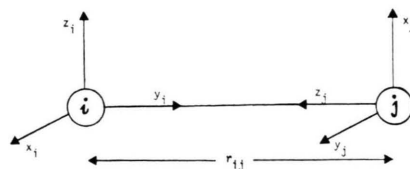


Fig. 1. The bond-stretching internal coordinate δr_{ij} .

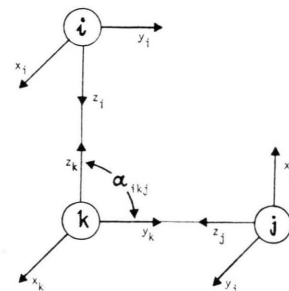


Fig. 2. The angle-bending internal coordinate $\delta \alpha_{ikj}$ ($\alpha_{ikj} = 90^\circ$).

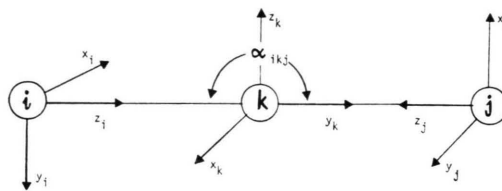


Fig. 3. The angle-bending internal coordinate $\delta \alpha_{ikj}$ ($\alpha_{ikj} = 180^\circ$).

one and two-center moment integrals of the type $\langle \Psi_I | X^\alpha Y^\beta Z^\gamma | \Psi_{II} \rangle$ has been recently presented¹² and a computer program specifically coded for the IBM 1620. Copies of the latter can be obtained from The Quantum Chemistry Program Exchange¹³ of Indiana University.

Acknowledgement

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Appendix A

The temperature dependence of vibronic intensities

The BOLTZMANN population of the a -th normal mode of the l -th vibrational level is given¹⁴ by

$$B_l = \exp(-\beta \hbar \sum_a \nu_a \nu_a^l) \cdot \prod_a [1 - \exp(-\beta \hbar \nu_a)] \quad (A1)$$

¹¹ M. TINKHAM, *Group Theory and Quantum Mechanics*, McGraw-Hill Book Co., Inc., New York 1964.

¹² W. A. YERANOS, *Z. Naturforsch.* **21a**, 1864 [1966].

¹³ Interested Europeans should write to Programmbibliothek, Deutsches Rechenzentrum, 6100 Darmstadt, Rheinstrasse 75, Germany (FRG).

and the mean square value of the normal coordinate Q_a is given¹⁵ by

$$\langle Q_a^2 \rangle_u = (v_a^l + \frac{1}{2}) \frac{1}{\gamma_a} \quad \text{where} \quad \gamma_a = \frac{4\pi^2 \nu_a}{h}. \quad (\text{A } 2)$$

Hence, we have

$$\sum_l B_l \langle Q_a^2 \rangle_u = \sum_l \exp(-\beta h \sum_a \nu_a v_a^l) \cdot \prod_a [1 - \exp(-\beta h \nu_a)] \cdot (v_a^l + \frac{1}{2}) \frac{1}{\gamma_a} \quad (\text{A } 3 \text{ a})$$

$$= \frac{1}{\gamma_a} \cdot \prod_a [1 - \exp(-\beta h \nu_a)] \cdot \left\{ \sum_l (v_a^l + \frac{1}{2}) \cdot \exp(-\beta h \sum_a \nu_a v_a^l) \right\} \quad (\text{A } 3 \text{ b})$$

$$= \frac{1}{\gamma_a} \cdot \prod_a [1 - \exp(-\beta h \nu_a)] \cdot \left\{ \sum_l v_a^l \cdot \exp(-\beta h \sum_a \nu_a v_a^l) + \frac{1}{2} \sum_l \exp(-\beta h \sum_a \nu_a v_a^l) \right\} \quad (\text{A } 3 \text{ c})$$

$$\text{and since} \quad \sum_l B_l = 1 = \sum_l \exp(-\beta h \sum_a \nu_a v_a^l) \cdot \prod_a [1 - \exp(-\beta h \nu_a)] \quad (\text{A } 4)$$

it is obvious then that if Eq. (4) is to hold

$$\sum_l \exp(-\beta h \sum_a \nu_a v_a^l) \equiv \left\{ \prod_a [1 - \exp(-\beta h \nu_a)] \right\}^{-1}. \quad (\text{A } 5)$$

Let us differentiate both sides of Eq. (5) with respect to ν_a . Upon doing so, we obtain

$$\begin{aligned} \sum_l (-\beta h \nu_a^l) \cdot \exp(-\beta h \sum_a \nu_a v_a^l) \cdot \exp(-\beta h \sum_{b \neq a} \nu_b v_b^l) \\ = [(-\beta h) \cdot \exp(-\beta h \nu_a)] \cdot [1 - \exp(-\beta h \nu_a)]^{-1} \left\{ \prod_a [1 - \exp(-\beta h \nu_a)] \right\}^{-1} \end{aligned} \quad (\text{A } 6 \text{ a})$$

which upon simplification and rearrangement gives

$$\sum_l \nu_a^l \cdot \exp(-\beta h \sum_a \nu_a v_a^l) = \exp(-\beta h \nu_a) \cdot [1 - \exp(-\beta h \nu_a)]^{-1} \left\{ \prod_a [1 - \exp(-\beta h \nu_a)] \right\}^{-1} \quad (\text{A } 6 \text{ b})$$

thus Eq. (A 3 c) becomes

$$\begin{aligned} \sum_l B_l \langle Q_a^2 \rangle_u = \frac{1}{\gamma_a} \prod_a [1 - \exp(-\beta h \nu_a)] \\ \cdot \left[\exp(-\beta h \nu_a) \cdot [1 - \exp(-\beta h \nu_a)]^{-1} \left\{ \prod_a [1 - \exp(-\beta h \nu_a)] \right\}^{-1} + \frac{1}{2} \sum_l \exp(-\beta h \sum_a \nu_a v_a^l) \right]. \end{aligned} \quad (\text{A } 7)$$

The last term of Eq. (7) is defined as the partition function¹⁶ for the vibration a and is given by

$$\Theta = \left\{ \prod_a [1 - \exp(-\beta h \nu_a)] \right\}^{-1} = \sum_l \exp(-\beta h \sum_l \nu_a v_a^l). \quad (\text{A } 8)$$

Hence substituting Eq. (8) in Eq. (7) and simplifying, we obtain

$$\sum_l B_l \langle Q_a^2 \rangle_u = \frac{1}{\gamma_a} \left(\frac{e^{-\beta h \nu_a}}{1 - e^{-\beta h \nu_a}} + \frac{1}{2} \right) = \frac{1}{2\gamma_a} \left(\frac{1 + e^{-\beta h \nu_a}}{1 - e^{-\beta h \nu_a}} \right). \quad (\text{A } 9)$$

The last equation reduces to the trigonometric¹⁷ relationship

$$\sum_l B_l \langle Q_a^2 \rangle_u = (1/2 \gamma_a) \operatorname{ctnh}(h \nu_a / 2 k T)$$

where ν_a is the frequency of vibration in cycles/sec.

¹⁴ E. B. WILSON JR., J. C. DECUS, and P. C. CROSS, *Molecular Vibrations*, McGraw-Hill Book Co., Inc., New York 1955, p. 164.

¹⁵ WILSON et al. ¹⁴, p. 290.

¹⁶ WILSON et al. ¹⁴, p. 165.

¹⁷ Multiplication of the numerator and denominator by $e^{+\beta h \nu_a / 2}$ gives

$$\frac{e^{+\beta h \nu_a / 2} + e^{-\beta h \nu_a / 2}}{e^{+\beta h \nu_a / 2} - e^{-\beta h \nu_a / 2}} = \frac{\cosh(h \nu_a / 2 k T)}{\sinh(h \nu_a / 2 k T)} = \operatorname{ctnh}(h \nu_a / 2 k T).$$