On the G sum rule formulation

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In 1952, Decius devised a rule relating the intensity sums of the fundamental vibrations of nonpolar isotopically related molecules.[1] Using the G sum rule of Crawford[2] as later written by King,[3]

$$\sum_i A_i/K = \sum_\alpha \xi_\alpha^2/m_\alpha - \Omega, \tag{1}$$

a more general formulation which includes rotational corrections can be easily obtained. In Eq. (1), A_i is the absorption coefficient of the Beer's law integrated over the frequencies of the fundamental band i, ξ_α is the effective charge defined by King,[3] m_α is the mass of atom α, Ω is a rotational correction depending on the atomic masses, the molecular geometry and the equilibrium dipole moment,[3] and $K = N\pi d_i v_i/3\,c^2\omega_i$ is a constant. N is the Avogadro number, d_i the degeneracy of band i, c the velocity of light in vacuum, v_i and ω_i the observed and the harmonic frequency, respectively, of band i.

Considering a hypothetical chemical reaction $\sum_S \mu_S S = 0$, where S stands for "substance" and μ_S for its stoichiometric coefficient, and Eq. (1), one may write

$$\sum_S \mu_S \sum_{i=1}^{t_S} A_{iS}/K = \sum_S \mu_S \left(\sum_{\alpha=1}^{n_S} \xi_{\alpha S}^2/m_\alpha - \Omega_S \right), \tag{2}$$

where t_S and n_S are the number of fundamental bands and atoms of molecule S, respectively. If all S molecules involved in the reaction are isotopically related, $n_S = n$ and $\xi_S = \xi$ for all species. Moreover, $\sum_S \mu_S = 0$. Thus, for isotopic substitution reactions,

$$\sum_S \mu_S \left(\Omega_S + \sum_{i=1}^{t_S} A_{iS}/K \right) = \left(\sum_S \mu_S \right) \left(\sum_{\alpha=1}^{n} \xi_\alpha^2/m_\alpha \right) = 0. \tag{3}$$

For all $\Omega_S = 0$, Eq. (3) is the Decius sum rule.[1] Although the unavailability of numerical data prevented a meaningful test of this rule in 1952, much more data are currently available, permitting us to judge the usefulness of this sum rule. Theoretical intensity sums and their corresponding experimental values are included in Table I for some molecules and their isotopic analogs for which reliable infrared intensities are known. In most cases, agreement is within reported experimental error.

It may be shown that the use of Eq. (3) in checking

TABLE I. Calculated and experimental values of $(K\Omega + \sum_i A_i)$ (km/mol).

Molecule	Reaction	Calculated[a]	Experimental
CH_3D	$1/2CH_4 + 1/2CD_2H_2 \rightarrow CH_3D$	88.6 ± 2.6	86.7 ± 1.9[b]
	$2/3CH_4 + 1/3CD_3H \rightarrow CH_3D$	88.5 ± 3.0	
	$3/4CH_4 + 1/4CD_4 \rightarrow CH_3D$	90.5 ± 2.6	
CD_3H	$1/2CD_4 + 1/2CD_2H_2 \rightarrow CD_3H$	61.6 ± 1.8	57.4 ± 2.9[b]
	$2/3CD_4 + 1/3CH_3D \rightarrow CD_3H$	62.2 ± 1.5	
	$3/4CD_4 + 1/4CH_4 \rightarrow CD_3H$	63.4 ± 1.7	
CH_2D_2	$1/2CH_4 + 1/2CD_4 \rightarrow CH_2D_2$	77.0 ± 2.2	73.2 ± 2.2[b]
	$2/3CD_3H + 1/3CH_4 \rightarrow CH_2D_2$	72.9 ± 2.9	
	$2/3CH_3D + 1/3CD_4 \rightarrow CH_2D_2$	74.4 ± 1.7	
	$1/4CH_4 + 1/4CH_3D + 1/4CD_3H + 1/4CD_4 \rightarrow CH_2D_2$	74.5 ± 2.3	
CH_3CH_2D	$1/2CH_3CH_3 + 1/2CH_2DCH_2D \rightarrow CH_3CH_2D$	185.8 ± 7.5	182.8 ± 9.0[c]
	$2/3CH_3CH_3 + 1/3CH_3CD_3 \rightarrow CH_3CH_2D$	187.4 ± 6.8	
CH_3CD_3	$1/2CH_3CH_3 + 1/2CD_3CD_3 \rightarrow CH_3CD_3$	153.2 ± 5.1	156.9 ± 10.9[c]
CH_2DCH_2D	$2/3CH_3CH_3 + 1/3CD_3CD_3 \rightarrow CH_2DCH_2D$	170.0 ± 5.0	169.0 ± 10.2[c]
CH_2DBr	$1/2CH_3Br + 1/2CHD_2Br \rightarrow CH_2DBr$	69.6 ± 2.2	67.6 ± 1.5[d]
	$2/3CH_3Br + 1/3CD_3Br \rightarrow CH_2DBr$	65.8 ± 1.8	
CHD_2Br	$1/2CD_3Br + 1/2CH_2DBr \rightarrow CHD_2Br$	55.9 ± 1.4	62.5 ± 2.0[d]
	$2/3CD_3Br + 1/3CH_3Br \rightarrow CHD_2Br$	55.0 ± 1.6	
$t\text{-}C_2H_2D_2$	$1/2C_2H_4 + 1/2C_2D_4 \rightarrow C_2H_2D_2$	97.6 ± 1.4	98.4 ± 1.3[e]
$c\text{-}C_2H_2D_2$	$1/2C_2H_4 + 1/2C_2D_4 \rightarrow C_2H_2D_2$	97.6 ± 1.4	109.9 ± 2.3[e]
$CHDCF_2$	$1/2CH_2CF_2 + 1/2CD_2CF_2 \rightarrow CHDCF_2$	581.7 ± 60.3	534.3 ± 8.8[f]

[a] Equation (3), see the text.
[b] See Ref. 5.
[c] See Ref. 6.
[d] See Ref. 7 for $\sum_i A_i$ and Ref. 8 for Ω.
[e] See Ref. 9.
[f] See Ref. 10 for $\sum_i A_i$; Ω was calculated by the authors.

consistency among intensity sums for a family of isotopically related molecules is equivalent to employing Eq. (1). For each molecule, Eq. (1) may be written as

$$\sum_{\alpha \neq H,D} \xi_\alpha^2/m_\alpha = -(p/m_H + q/m_D)\xi_H^2$$

$$+ \left(\Omega + \sum_i A_i/K\right), \qquad (4)$$

where p and q are, respectively the number of H and D atoms in the molecule. Considering the two quantities ξ_H^2 and

$\Sigma_{\alpha \neq H,D}\xi_\alpha^2/m_\alpha$ as variables, Eq. (4) is the equation of a straight line.[4] The coordinates of the intersection of two or more lines, each line corresponding to one isotopically related molecule, are the isotopically invariant ξ_H^2 and $\Sigma_{\alpha \neq H,D}\xi_\alpha^2/m_\alpha$ values. These coordinates may be algebraicly obtained using the equations

$$\xi_H^2 = \frac{(\Omega_2 + \Sigma_{i=1}^{t_2} A_{i2}/K) - (\Omega_1 + \Sigma_{i=1}^{t_1} A_{i1}/K)}{(p_2 - p_1)/m_H + (q_2 - q_1)/m_D} \qquad (5)$$

and

$$\sum_{\alpha \neq H,D} \xi_\alpha^2/m_\alpha = \frac{(p_2/m_H + q_2/m_D)(\Omega_1 + \Sigma_{i=1}^{t_1} A_{i1}/K) - (p_1/m_H + q_1/m_D)(\Omega_2 + \Sigma_{i=1}^{t_2} A_{i2}/K)}{(p_2 - p_1)/m_H + (q_2 - q_1)/m_D}. \qquad (6)$$

Substituting the above expressions for ξ_H^2 and $\Sigma_{\alpha \neq H,D}\xi_\alpha^2/m_\alpha$ in Eq. (4), the $(\Omega_3 + \Sigma_{i=1}^{t_3} A_{i3}/K)$ value of a third molecule may be obtained from the $(\Omega_1 + \Sigma_{i=1}^{t_1} A_{i1}/K)$, $(\Omega_2 + \Sigma_{i=1}^{t_2} A_{i2}/K)$, p_1, p_2, p_3, q_1, q_2, and q_3 values. The expression for $(\Omega_3 + \Sigma_{i=1}^{t_3} A_{i3}/K)$ may be written

$$((p_1 - p_2)/m_H + (q_1 - q_2)/m_D)\left(\Omega_3 + \sum_{i=1}^{t_3} A_{i3}/K\right) + ((p_2 - p_3)/m_H + (q_2 - q_3)/m_D)\left(\Omega_1 + \sum_{i=1}^{t_1} A_{i1}/K\right)$$

$$+ ((p_3 - p_1)/m_H + (q_3 - q_1)/m_D)\left(\Omega_2 + \sum_{i=1}^{t_2} A_{i2}/K\right) = 0. \qquad (7)$$

It is easily shown that the coefficients in Eq. (7) are, respectively, proportional to the stoichiometric coefficients μ_3, μ_1, and μ_2 of a hypothetical reaction interrelating the three isotopically related molecules, i.e., $\Sigma_{i=1}^3 \mu_s S = 0$. Thus, Eq. (7) is an extension of Eq. (3) for three molecules and, using identical data for two isotopically related molecules, identical $(\Omega + \Sigma_i A_i/K)$ values of a third molecule are obtained by means of both Eqs. (4) or (1) and (3).

Equation (3) provides perhaps the easiest way of performing a G sum rule check for the fundamental intensities of a family of three or more isotopically related molecules. All that needs be done is to calculate the stoichiometric coefficients of any hypothetical reaction relating these molecules. Each linear independent hypothetical reaction corresponds to an independent check and, for each reaction, symmetry species may be treated separately. For polar molecules, Ω may be easily calculated using Eq. (9) of King's paper.[3] To separately check each symmetry species, Ω must be partitioned as

$$\Omega = \Omega_{XX} + \Omega_{YY} + \Omega_{ZZ}, \qquad (8)$$

where

$$\Omega_{XX} = P_Z^2/I_{YY} + P_Y^2/I_{ZZ}, \qquad (9)$$

$$\Omega_{YY} = P_Z^2/I_{XX} + P_X^2/I_{ZZ}, \qquad (10)$$

and

$$\Omega_{ZZ} = P_Y^2/I_{XX} + P_X^2/I_{YY}. \qquad (11)$$

In the above equations, P_X, P_Y, and P_Z are the components of the molecular equilibrium dipole moment, whereas I_{XX}, I_{YY}, and I_{ZZ} are the molecular moments of inertia in relation to X, Y, and Z principal axes, respectively.

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