On the $G$ sum rule formulation

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(Received 24 August 1983; accepted 29 December 1983)

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,\(^3\)

$$
\sum \frac{A_j}{K} = \sum \xi_{\alpha}^2 / m_\alpha - \Omega,
$$

(1)
a more general formulation which includes rotational corrections can be easily obtained. In Eq. (1), $A_j$ is the absorption coefficient of the Beer’s law integrated over the frequencies of the fundamental band $i$, $\xi_{\alpha}$ is the effective charge defined by King,\(^3\) $m_\alpha$ is the mass of atom $\alpha$, $\Omega$ 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 $\omega_i$ 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 $\mu_S$ for its stoichiometric coefficient, and Eq. (1), one may write

$$
\sum_S \mu_S \sum_{i=1}^{n_s} \frac{A_{iS}}{K} = \sum_S \mu_S \left( \sum_{\alpha=1}^{n_\alpha} \frac{\xi_{\alpha}^2}{m_\alpha} - \Omega_S \right),
$$

(2)
where $n_s$ and $n_\alpha$ are the number of fundamental bands and atoms of molecule $S$, respectively. If all $S$ molecules involved in the reaction are isotopically related, $n_\alpha = n$ and $\xi_{\alpha}^2 = \xi$ for all species. Moreover, $\sum_S \mu_S = 0$. Thus, for isotopic substitution reactions,

$$
\sum_S \mu_S \left( \Omega_S + \sum_{i=1}^{n_s} \frac{A_{iS}}{K} \right) = \left( \sum_S \mu_S \right) \left( \sum_{\alpha=1}^{n_\alpha} \frac{\xi^2}{m_\alpha} \right) = 0.
$$

(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>
<thead>
<tr>
<th>Molecule</th>
<th>Reaction</th>
<th>Calculated*</th>
<th>Experimental</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$D</td>
<td>1/2CH$_3$ + 1/2CD$_3$H $</td>
<td></td>
<td></td>
</tr>
</tbody>
</table><p>ightarrow$ CH$_3$D | 88.6 ± 2.6 | 86.7 ± 1.9$^b$ |
|         | 2/3CH$_3$ + 1/3CD$_3$H $ightarrow$ CH$_3$D | 88.5 ± 3.0 | 87.7 ± 1.6$^b$ |
|         | 3/4CH$_3$ + 1/4CD$_3$H $ightarrow$ CH$_3$D | 90.5 ± 2.6 | |
| CD$_3$H  | 1/2CD$_3$ + 1/2H$_2$ $ightarrow$ CD$_3$H | 61.6 ± 1.8 | 57.4 ± 2.6$^b$ |
|         | 2/3CD$_3$ + 1/3H$_2$ $ightarrow$ CD$_3$H | 62.2 ± 1.5 | 61.9 ± 2.6$^b$ |
|         | 3/4CD$_3$ + 1/4H$_2$ $ightarrow$ CD$_3$H | 63.4 ± 1.7 | 63.2 ± 2.6$^b$ |
| CH$_3$D  | 1/2CH$_3$ + 1/2CD$_3$H $ightarrow$ CH$_3$D | 77.0 ± 2.2 | 73.2 ± 2.2$^b$ |
|         | 2/3CD$_3$ + 1/3CH$_3$H $ightarrow$ CH$_3$D | 72.9 ± 2.9 | 71.5 ± 2.1$^b$ |
|         | 3/4CD$_3$ + 1/4CH$_3$H $ightarrow$ CH$_3$D | 74.4 ± 1.7 | 74.4 ± 2.3 |
|         | 1/4CH$_3$ + 1/4CD$_3$H + 1/4CD$_3$H + 1/4CD$_3$H | 74.5 ± 2.3 | |
| CH$_3$CH$_2$D | 1/2CH$_3$CH$_2$ + 1/2CD$_3$H $ightarrow$ CH$_3$CH$_2$D | 185.8 ± 7.5 | 182.8 ± 9.0$^e$ |
|         | 2/3CH$_3$CH$_2$ + 1/3CD$_3$H $ightarrow$ CH$_3$CH$_2$D | 187.4 ± 6.8 | 186.5 ± 7.0$^e$ |
| CH$_3$CD$_2$ | 1/2CD$_3$ + 1/2CH$_3$CH$_2$H $ightarrow$ CH$_3$CD$_2$ | 153.2 ± 5.1 | 156.9 ± 10.9$^e$ |
|         | 2/3CD$_3$ + 1/3CH$_3$CH$_2$H $ightarrow$ CH$_3$CD$_2$ | 170.0 ± 5.0 | 169.0 ± 10.2$^e$ |
| CH$_3$DBr | 1/2CD$_3$ + 1/2CD$_3$Br $ightarrow$ CH$_3$DBr | 69.6 ± 2.2 | 67.6 ± 1.6$^d$ |
|         | 2/3CD$_3$ + 1/3CD$_3$Br $ightarrow$ CH$_3$DBr | 65.8 ± 1.8 | 63.2 ± 2.0$^d$ |
| CHD$_2$Br | 1/2CD$_3$ + 1/2CD$_3$Br $ightarrow$ CHD$_2$Br | 55.9 ± 1.4 | 62.5 ± 2.0$^d$ |
|         | 2/3CD$_3$ + 1/3CD$_3$Br $ightarrow$ CHD$_2$Br | 55.0 ± 1.6 | 60.9 ± 2.0$^d$ |
| t-C$_3$H$_2$D | 1/2CD$_3$ + 1/2CD$_3$H $ightarrow$ t-C$_3$H$_2$D | 97.6 ± 1.4 | 98.4 ± 1.3$^e$ |
|         | 1/2CD$_3$ + 1/2CD$_3$H $ightarrow$ t-C$_3$H$_2$D | 97.6 ± 1.4 | 98.4 ± 1.3$^e$ |
| CHDCF$_2$ | 1/2CH$_2$CF$_2$ + 1/2CD$_3$H $ightarrow$ CHDCF$_2$ | 581.7 ± 60.3 | 534.3 ± 8.8$^f$ |</p>

* Equation (3), see the text.
* See Ref. 5.
* See Ref. 6.
* See Ref. 7 for $\Omega$, $A_j$, and Ref. 8 for $\Omega$.
* See Ref. 9.
* See Ref. 10 for $\Omega$, $A_j$; $\Omega$ 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

\[
\frac{\sum_{\alpha \neq H, D} \xi_{\alpha}^2}{m_\alpha} = -\left(\frac{p}{m_H} + \frac{q}{m_D}\right) \xi_H^2 + \left(\Omega + \sum_{i} A_i / K\right),
\]  

where \(p\) and \(q\) are, respectively the number of \(H\) and \(D\) atoms in the molecule. Considering the two quantities \(\xi_H^2\) and \(\sum_{\alpha \neq H, D} \xi_{\alpha}^2 / m_\alpha\) 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 \(\xi_H^2\) and \(\sum_{\alpha \neq H, D} \xi_{\alpha}^2 / m_\alpha\) values. These coordinates may be algebraically obtained using the equations

\[
\xi_H^2 = \frac{\left(\frac{p_2 - p_1}{m_H} + \frac{q_2 - q_1}{m_D}\right)}{\left(p_2 - p_1\right) m_H + \left(q_2 - q_1\right) m_D}
\]

and

\[
\sum_{\alpha \neq H, D} \xi_{\alpha}^2 / m_\alpha = \left(p_2 / m_H + q_2 / m_D\right) \left(p_1 / m_H + q_1 / m_D\right)\left(\xi_H^2 - \sum_{i} A_i / K\right).
\]

Substituting the above expressions for \(\xi_H^2\) and \(\sum_{\alpha \neq H, D} \xi_{\alpha}^2 / m_\alpha\) in Eq. (4), the \(\Omega + \sum_{i} A_i / K\) value of a third molecule may be obtained from the \(\left(p_1 + \sum_{i=1}^{3} A_i / K\right)\left(p_2 - p_3\right) m_H + \left(q_2 - q_3\right) m_D\left(\xi_H^2 - \sum_{i} A_i / K\right)\)

\[
+ \left(\frac{p_3 - p_1}{m_H} + \frac{q_3 - q_1}{m_D}\right) \left(p_2 / m_H + q_2 / m_D\right) = 0.
\]

It is easily shown that the coefficients in Eq. (7) are, respectively, proportional to the stoichiometric coefficients \(\mu_2, \mu_1,\) and \(\mu_2\) of a hypothetical reaction interrelating the three isotopically related molecules, i.e., \(\sum_{i=1}^{3} \mu_i S = 0\). Thus, Eq. (7) is an extension of Eq. (3) for three molecules and, using identical data for two isotopically related molecules, identical \((\Omega + \sum A_i / K)\) 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, \(\Omega\) may be easily calculated using Eq. (9) of King's paper.\(^3\) To separately check each symmetry species, \(\Omega\) must be partitioned as

\[
\Omega = \Omega_{XX} + \Omega_{YY} + \Omega_{ZZ},
\]

where

\[
\begin{align*}
\Omega_{XX} & = P_X I_{YY} + P_Y I_{ZZ}, \\
\Omega_{YY} & = P_Y I_{XX} + P_Z I_{ZZ}, \quad \text{(9)} \\
\Omega_{ZZ} & = P_Z I_{XX} + P_Y I_{YY} \quad \text{(10)}
\end{align*}
\]

and

\[
\begin{align*}
\Omega_{XX} & = P_X I_{XX}, \\
\Omega_{YY} & = P_Y I_{YY}, \quad \text{(11)}
\end{align*}
\]

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.

The authors are very grateful to Professor Roy E. Bruns, for his suggestions. Financial support from FINEP is acknowledged. M.M.C.F. is indebted to CNPq for a fellowship.