On Some Theoretical Aspects of the 1-Type Doubling Constant $q_e$:
Application to XYZ ($C_{\infty v}$) Type Molecules

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The relationship between the 1-type doubling constant $q_e$ and the centrifugal distortion constant $D_e$ and the range of real values of $q_e$ for XYZ ($C_{\infty v}$) type molecules, is derived in detail. The experimental value of $q_e$ for many molecules is found to be in the neighborhood of its minimum. The usefulness of $q_e$ in fixing a unique and accurate force field for XYZ ($C_{\infty v}$) type molecules is also discussed. A brief discussion of the nature of the errors arising due to the use of $D_e$, $B_e$ and $r_1$ in the calculation (for $q_e$) is presented. The study of the mass effect on $q_e$ is also reported.

Introduction

The determination of the 1-doubling constant $q_{e1}$ ($e_1 = \text{vibrational state}$) for symmetric tops (including linear) constitutes an important aspect of structural chemistry. The 1-doubling constant determined from high resolution far infrared and microwave spectra is due to the excitation of degenerate (bending) modes and reflects the interaction between vibrational and rotational angular momenta. To a first approximation 1, the components are split by an amount given by

$$\Delta \nu = q_e (v_1 + 1) J (J + 1)$$

where $v_1$ and $J$ are the vibrational and the rotational quantum numbers respectively and $q_e$ is the 1-doubling constant at the equilibrium configuration.

The 1-doubling constant has successfully been used to determine the intramolecular force field (both harmonic and anharmonic) 2–5. In recent years, 1-doubling constants have been determined very accurately 5–11, so that they can be used as additional data in fixing the force field. It is the aim of the present communication to discuss some hitherto unknown aspects of the 1-doubling constant $q_e$ for XYZ ($C_{\infty v}$) type molecules, only for which a large number of data on $q_e$ is reported in literature.

Extremal Properties of $q_e$

The 1-doubling constant $q_e$ for XYZ ($C_{\infty v}$) type molecules can be calculated using the relation

$$q_e = -(2 B_e^2/\omega_2)(1 + 4 (\zeta_{12}^v \zeta_{23}^v)^2 \omega_2^2 / (\omega_1^2 - \omega_2^2)^{-1} + 4 \omega_2^2 (\omega_2 - \omega_2^2)^{-1})$$

where the $\omega$'s are the harmonic vibrational frequencies ($\omega_2$ pertains to the degenerate bending mode), $B_e$, the equilibrium rotational constant, $h$ the Planck’s constant and $(\zeta_{ij}^v)^2$ are second order Coriolis coupling constants ($z$ axis is assumed to be the equilibrium molecular axis). Using the relation

$$(\zeta_{12}^v)^2 + (\zeta_{23}^v)^2 = 1$$

one may rewrite Eq. (2) as

$$q_e = -(2 B_e^2/\omega_2)[1 + 4 \omega_2^2 (\omega_2 - \omega_2^2)^{-1} + 4 \omega_2^2 (\omega_2 - \omega_2^2)^{-1}]$$

Thus the extremal values correspond to those of $(\zeta_{ij}^v)^2$ (which are 0 and +1) and the extremal values themselves are given by (assuming $\omega_1 > \omega_2$ without any loss of generality)

$$(q_e)_{\text{min}} = -(2 B_e^2/\omega_2)[1 + 4 \omega_2^2 (\omega_2 - \omega_2^2)^{-1}]$$

$$(q_e)_{\text{max}} = -(2 B_e^2/\omega_2)[1 + 4 \omega_2^2 (\omega_2 - \omega_2^2)^{-1}]$$

In order to see whether the experimental value of $q_e$ for XYZ ($C_{\infty v}$) type molecules is in the neighborhood of its extrema, we calculated the maximal and the minimal limits of $q_e$ and the results are presented in Table 1.

Relation between $q_e$ and $D_e$

It was already shown 12 that there exists a relationship between the centrifugal distortion constants and the Coriolis coupling constants. For linear XYZ type molecules, one has

$$D_e = 4 B_e^3 \left[ (\omega_2^2)^{-1} \left( 1 - (\zeta_{12}^v)^2 \right) + (\omega_2^2)^{-1} \left( 1 - (\zeta_{23}^v)^2 \right) \right].$$

If one assumes that $\omega_1 > \omega_2$ (as mentioned earlier), it can be easily shown that $D_e$ is maximum when
\((\zeta_{23}^{2})^{2} = 0\). As seen from Eq. (4), this corresponds to \((q_{e})_{\text{min}}\). Since, it is desirable to present the general relationship between \(q_{e}\) and \(D_{e}\) for this molecular type, we give the result here.

i.e. \(q_{e} = (2 B_{e}^{2}/\omega_{2}) \left[1 + 4 \omega_{2}^{2}(\omega_{3}^{2} - \omega_{2}^{2})^{-1} - 4 \omega_{1}^{2} \omega_{2}^{2} \omega_{3}^{2} (\omega_{3}^{2} - \omega_{2}^{2})^{-1} (\omega_{2}^{2} - \omega_{3}^{2})^{-1} \right] \) \(= F_{n}^{3} - (1/O_{1}^{2})\) . (7)

Equation (7) can be used to determine \(q_{e}\) from \(D_{e}\) and vice versa and should provide a check on the experimental results. Since, in many cases, \(q_{e}\) has not been determined \(3\) (only \(q_{s}\) for different excited states of the ‘\(\omega_{2}\)’ vibration are known), Eq. (7) could be used in this direction (the influence of vibration on \(D_{e}\) in contrast to that on \(q_{e}\)) in general negligible \(1\). In order to illustrate the usefulness of Eq. (7), we have presented the numerical results for \(q_{e}\) determined from the experimental values of \(D_{e}\) for many \(\text{XYZ (C}_{\infty v})\) type molecules in Table 1.

### Unique Solution of Force Constants

When one has the frequencies of two isotopes, one gets two linear relations of the following form in terms of the force constants

\[ i.e. \quad \lambda_{1}^{(i)} + \lambda_{3}^{(i)} = G_{11}^{(i)} F_{11}^{(i)} + 2 G_{13}^{(i)} F_{13}^{(i)} + G_{33}^{(i)} F_{33}^{(i)} \]

\[ \lambda_{1}^{(i)} + \lambda_{3}^{(i)} = G_{11}^{(i)} F_{11}^{(i)} + 2 G_{13}^{(i)} F_{13}^{(i)} + G_{33}^{(i)} F_{33}^{(i)} \]

(8)

Hence, another linear relation is needed to get a unique solution for the force constants. The problem of computing a single set of force constants for \(n = 2\) cases has been analysed in recent years, quite extensively by Hoy et al. \(13\) and Müller et al. \(14\), who have suggested the use of isotopic shifts arising out of asymmetric substitution, bonded mean amplitude of vibration \(13\) and the inertia defect \(14\) for obtaining another linear equation, analogous to Equation (8). For linear XYZ type molecules, the 1-doubling constant \(q_{e}\) can be used to derive a linear relation in the force constants (\(\Sigma^{2}\)). The 1-doubling constant \(q_{e}\) is connected with the force constants through the relation \(15\)

\[ \lambda_{1} (\zeta_{23}^{2})^{2} + \lambda_{3} (\zeta_{23}^{2})^{2} = F_{23} \lambda_{2}^{-1} [F_{11} (\zeta_{23}^{2})]^{2} + 2 F_{13} (\zeta_{23}^{2}) + F_{33} (\zeta_{23}^{2})^{2} \]

(9)

[the zetas are connected with \(q_{e}\) through Equation (2)].

### Table 1. Extremal values and those calculated from \(D_{e}\) of \(q_{e}\) in MHz of some XYZ (\(\text{C}_{\infty v}\)) type molecules.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>(q_{e}) (max.)</th>
<th>(q_{e}) (min.)</th>
<th>(q_{e}) (expt.)</th>
<th>(q_{e}) from (D_{e}) (expt.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^{32}\text{SCO})</td>
<td>15.26 (a)</td>
<td>6.00 (a)</td>
<td>6.21 (b)</td>
<td>6.02 (c)</td>
</tr>
<tr>
<td>(^{35}\text{SeCO})</td>
<td>15.09 (e)</td>
<td>2.83 (e)</td>
<td>3.15 (d)</td>
<td>3.12 (e)</td>
</tr>
<tr>
<td>(^{35}\text{ICN})</td>
<td>14.73 (a)</td>
<td>7.06 (a)</td>
<td>7.47 (d)</td>
<td>7.36 (a), (f)</td>
</tr>
<tr>
<td>(^{79}\text{BrCN})</td>
<td>10.14 (a)</td>
<td>3.65 (a)</td>
<td>3.91 (d)</td>
<td>3.83 (a), (f)</td>
</tr>
<tr>
<td>(^{81}\text{BrCN})</td>
<td>10.02 (e)</td>
<td>3.53 (e)</td>
<td>3.71 (d)</td>
<td>3.58 (f)</td>
</tr>
<tr>
<td>(^{12}\text{C}_{14}\text{N})</td>
<td>8.18 (e)</td>
<td>2.46 (e)</td>
<td>2.69 (d)</td>
<td>2.87 (f)</td>
</tr>
<tr>
<td>(^{12}\text{C}_{15}\text{N})</td>
<td>726.18 (e)</td>
<td>202.00 (e)</td>
<td>205.23 (d)</td>
<td>202.18 (i)</td>
</tr>
<tr>
<td>(^{12}\text{C}_{14}\text{N})</td>
<td>210.73 (m)</td>
<td>181.23 (m)</td>
<td>181.47 (h)</td>
<td>181.45 (n)</td>
</tr>
<tr>
<td>(^{12}\text{C}_{15}\text{N})</td>
<td>200.69 (m)</td>
<td>171.46 (m)</td>
<td>171.60 (h)</td>
<td>171.62 (n)</td>
</tr>
</tbody>
</table>

\(a\) This corresponds to \(B_{0}\).
\(b\) This value of \(q_{e}\) is taken from Ref. \(3\).
\(c\) Value calculated from \(D_{e}\) using the frequencies given in Ref. \(3\).
\(d\) This corresponds to \(q_{e}\) of Ref. \(3\).
\(e\) This corresponds to \(B_{e}\).
\(f\) Value calculated using \(D_{e}\), and the frequencies given by A. Ruoff, Spectrochim. Acta 26 A, 545 [1970].
\(g\) For the experimental values see, J. B. Simpson, J. G. Smith, and D. H. Whiffen, J. Mol. Spectrosc. 44, 558 [1972].
\(h\) This value of \(q_{e}\) is from Ref. \(15\).
\(i\) Calculated using \(B_{0}\), \(D_{e}\), and \(\omega_{j}\) (see Refs. \(15, 19\) for the experimental results).
\(j\) Calculated from \(B_{0}\), \(D_{e}\), and \(\omega_{j}\).
\(k\) Calculated from \(B_{e}\), \(D_{e}\), and \(\omega_{j}\); the anharmonic frequencies \(\omega_{j}\) (gas phase) may be found in the work of J. Pacansky and G. V. Calder, J. Mol. Struct. 14, 363 [1972].
\(l\) Calculated using \(B_{0}\) and \(\omega_{j}\).
\(m\) Computed from \(B_{0}\) and \(\omega_{j}\).
\(n\) Corresponds to \(B_{e}\), \(D_{e}\), and \(\omega_{j}\).
\(p\) Determined using \(B_{0}\) and \(\omega_{j}\).
\(q\) Corresponds to \(B_{0}\), \(D_{e}\), and \(\omega_{j}\).
\(r\) Calculated using \(B_{0}\) and \(\omega_{j}\).
\(s\) Estimated from \(B_{0}\), \(D_{e}\), and \(\omega_{j}\).
As seen from the results given in Table 1, the experimental value of \( q_e \) is in the neighbourhood of its minimum. This also implies that the centrifugal distortion constant \( D_e \) is nearly a maximum for this molecular type.\(^{16,17}\) Eq. (5) can be used to define the boundaries of \( q_e \), so that it serves as a check on the experimental results. Since the value of \( q_e \) is nearly minimal for many XYZ (C\(_x\)) type molecules, we tried to see if this constraint (i.e. \( q_e \) is a minimum) could be used to determine reasonably approximate values of the force constants for the \( \Sigma^+ \) species. But, the values of the force constants thus obtained are found to be quite different from those reported in literature. This is not unexpected, since it was already shown\(^{16,17}\) that the condition that \( D_e \) is a maximum does not lead to physically meaningful results for the force constants. Our results indicate that \( q_e \) is not a very sensitive function of the force constants and hence approximate force field data could be employed to evaluate reasonably accurate value of \( q_e \). This is because, the terms \((\omega_1^2 - \omega_2^2)^{-1}, (\omega_3^2 - \omega_2^2)^{-1}\) and \((B_e^2/\omega_2)\) appearing in Eq. (2) are all small, so that even large errors in the values of the zetas (and hence those in the values of the force constants) cause only relatively small uncertainties in the value of \( q_e \).

Table 1 also indicates the usefulness of the general relationship between the 1-doubling constant \( q_e \) and the centrifugal distortion constant \( D_e \) derived in this paper. Thus, it can be noted that the experimental value of \( D_e \) for FCN can not be correct, since it leads to a value of \( q_e \) less than its minimum. Since, at this stage, it becomes important to assess the nature of the general errors involved in \( q_e \) determined using Eq. (7), we present below a brief discussion of this point.

The errors in \( q_e \) arise due to three factors, namely the use of (i) \( D_0 \) or \( D_e \) in place of \( D_e \), (ii) \( B_0 \) or \( B_e \) in place of \( B_e \), and (iii) \( \nu_1 \) in place of \( \nu_1 \). Considering Eq. (7), one may write

\[
q_e = a D_e + b
\]

where

\[
a = (-2/B_e \omega_2) \omega_1^2 \omega_2^2 \omega_3^2 \\
\times (\omega_1^2 - \omega_2^2)^{-1} (\omega_3^2 - \omega_2^2)^{-1}
\]

and

\[
b = (2 B_e^2 / \omega_2^2) [1 + 4 \omega_2^2 (\omega_2^2 - \omega_3^2)^{-1} \omega_2^2 \omega_3^2 (\omega_1^2 - \omega_2^2)^{-1} (\omega_3^2 - \omega_2^2)^{-1}]
\]

As can be easily seen \( a \gg b \). Hence, it is clear that even a small error in \( D_e \) (absolute error) will cause a large deviation in \( q_e \). However, one finds

\[
\Delta q_e/q_e = a (\Delta D_e) (a D_e + b)^{-1} \\
= (\Delta D_e/D_e) (1 + b/a D_e)^{-1}
\]

where \( \Delta q_e \) and \( \Delta D_e \) represent the absolute errors in \( q_e \) and \( D_e \) respectively. Since \((b/a D_e)\) is negative and numerically \( > 1\), it follows that the sign of \( \Delta q_e \) is opposite to that of \( \Delta D_e \). As \((b + a D_e)\) is small, the relative errors involved (in magnitude) in \( q_e \) and \( D_e \) are comparable. The results presented in Table 1 for HCN and DCN confirm this conclusion.

The dependence of \( q_e \) on \( B_e \) can be studied by rewriting Eq. (7) in the form

\[
q_e = a' B_e^2 + b'/B_e
\]

where \( a' \) and \( b' \) are constants (\( a' \) depends on the frequencies only and \( b' \) depends both on the frequencies and the centrifugal distortion constant; \( a' \) is positive and \( b' \) is negative). No general and exact dependence of \( q_e \) on \( B_e \) can be given [see Eq. (13)], but an approximate one can be derived from Eq. (13), if \((\Delta B_e/B_e) \ll 1\). In this case, one obtains

\[
q_e + \Delta q_e = a' (B_e + \Delta B_e)^2 + b' (1/B_e - (\Delta B_e/B_e)^2)
\]

Hence, we get

\[
\Delta q_e \approx [2 a' B_e \Delta B_e - b' \Delta B_e/B_e^2]
\]

Equation (16) shows that \( \Delta q_e \) is positive if \( \Delta B_e \) is positive. This, in other words, means that an increase in \( B_e \) causes an increase in the value of \( q_e \). Since \( B_e > B_e \) (including \( B_f \)), the use of \( B_e \) in place of \( B_e \) leads to a smaller value of \( q_e \). One important point is to be noted here. As seen from Eq. (12) and (16), the effect of using \( D_e \) in place of \( D_e \) and \( B_e \) in place of \( B_e \) acts in the same direction, namely to cause a decrease in the value of \( q_e \). This implies that the use of \( D_e \) and \( B_e \) in Eq. (7) would lead to a value of \( q_e \) lesser than its actual value. This is in agreement with the results given in Table 1 (e.g. HCN and DCN). The error involved in \( q_e \) due to the use of the observed (anharmonic) frequencies instead of the harmonic ones can not be ascertained easily, since the equation is complicated. It is however found from the numerical results that the error involved in this case is not high when the difference
$(\omega_i - \omega_i)$ is small (e.g. non hydrides). In the case of HCN and DCN, however, the use of $\omega_i$ in place of $\omega_j$ leads to large deviations from the experimental results. In conclusion, it may be said that the above errors (due to the use of $D_e$, $B_e$ and $\omega_j$) do not in general exceed 5%, and hence one can employ $D_e$, $B_e$ and $\omega_j$ (in cases where $D_e$, $B_e$ and $\omega_j$ are not known) to compute reliable values of $q_e$. Perfect agreement with the experimental results (for $q_e$) is however found when $D_e$, $B_e$ and $\omega_e$ are used (in cases where $D_e$, $B_e$ and $\omega_e$ are not known) to calculate $q_e$ (c.f. the results for $D^{12}\text{C}^{14}\text{N}$ and $D^{12}\text{C}^{15}\text{N}$; the $B_e$ values for these molecules were estimated using Eq. (6) and the results presented in Refs. 18–19. In all cases except FCN, the compatibility of $D_e$ (or $D_e$) and $q_e$ is good. As noted earlier, the value of the centrifugal distortion constant for FCN may not be very accurate.

Figure 1 shows the variation of $q_e$ as a function of the mass ratio ($m_x/m_z$) for a number of XCZ linear type molecules. It might be noted that this curve is similar to the one corresponding to the first order Coriolis coupling constant (mainly for $XY_4$ ($T_1$) type molecules) reported first by Cyvin et al. 20 and explained, later, theoretically by Müller et al. 21.

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