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 neighbourhood 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_v, B_v and v_i 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 l-doubling constant q_{v_i} (v_i = vibrational state) for symmetric tops (including linear) constitutes an important aspect of structural chemistry. The l-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

$$\Delta\nu = q_e\,(v_i+1)\,J(J+1) \qquad (1)$$

where v_i and J are the vibrational and the rotational quantum numbers respectively and q_e is the l-doubling constant at the equilibrium configuration.

The l-doubling constant has successfully been used to determine the intramolecular force field (both harmonic and anharmonic) [2–5]. In recent years, l-doubling constants have been determined very accurately [3, 6–11], 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 l-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 l-doubling constant q_e for XYZ ($C_{\infty v}$) type molecules can be calculated using the relation

$$q_e = (2B_e^2/\omega_2)\,[1 + 4(\zeta_{12}^{y})^2\,\omega_2^2\,(\omega_1^2-\omega_2^2)^{-1} + 4(\zeta_{23}^{y})^2\,\omega_2^2\,(\omega_3^2-\omega_2^2)^{-1}] \qquad (2)$$

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where the 'ω's are the harmonic vibrational frequencies (ω_2 pertains to the degenerate bending mode), 'B_e', the equilibrium rotational constant, 'h' the Planck's constant and $(\zeta_{ij}^{y})^2$ are second order Coriolis coupling constants (z axis is assumed to be the equilibrium molecular axis). Using the relation

$$(\zeta_{12}^{y})^2 + (\zeta_{23}^{y})^2 = 1 \qquad (3)$$

one may rewrite Eq. (2) as

$$q_e = (2B_e^2/\omega_2)\,[1 + 4\omega_2^2(\omega_1^2-\omega_2^2)^{-1} + 4\omega_2^2(\zeta_{23}^{y})^2 \cdot\{(\omega_3^2-\omega_2^2)^{-1} - (\omega_1^2-\omega_2^2)^{-1}\}]\,. \qquad (4)$$

Thus the extremal values correspond to those of $(\zeta_{23}^{y})^2$ (which are 0 and +1) and the extremal values themselves are given by (assuming $\omega_1 > \omega_3$ without any loss of generality)

$$(q_e)_{\min} = (2B_e^2/\omega_2)\,[1 + 4\omega_2^2\,(\omega_1^2-\omega_2^2)^{-1}]\,,$$
$$(q_e)_{\max} = (2B_e^2/\omega_2)\,[1 + 4\omega_2^2\,(\omega_3^2-\omega_2^2)^{-1}]\,. \qquad (5)$$

In order to see whether the experimental value of q_e for XYZ ($C_{\infty v}$) type molecules is in the neighbourhood 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

$$D_e = 4B_e^3\,[(\omega_1^2)^{-1}\{1-(\zeta_{12}^{y})^2\} + (\omega_3^2)^{-1}\{1-(\zeta_{23}^{y})^2\}]\,. \qquad (6)$$

If one assumes that $\omega_1 > \omega_3$ (as mentioned earlier), it can be easily shown that D_e is maximum when

Molecule	q_e (max.)	q_e (min.)	q_e (expt.)	q_e from D_e (expt.)
^{32}SCO	15.26 [a]	6.00 [a]	6.21 [b]	6.02 [c]
SeCO	12.59 [e]	2.83 [e]	3.15 [d]	3.12 [c]
FCN	30.72 [e]	19.04 [e]	19.68 [d]	17.93 [f]
$^{35}ClCN$	15.10 [a] (15.04) [e]	7.06 [a] (7.04) [e]	7.47 [d]	7.36 [a,f] (7.27) [f]
$^{37}ClCN$	14.73 [a] (14.67) [e]	6.78 [a] (6.75) [e]	7.18 [d]	7.01 [a,f] (6.93) [f]
$^{79}BrCN$	10.14 [a] (10.11) [e]	3.65 [a] (3.64) [e]	3.91 [d]	3.83 [a,f] (3.79) [f]
$^{81}BrCN$	10.02 [e]	3.53 [e]	3.71 [d]	3.58 [f]
ICN	8.18 [e]	2.46 [e]	2.69 [d] (2.66) [d,g]	2.87 [f]
$H^{12}C^{14}N$	275.58 [e]	214.02 [e]	217.38 [h]	214.15 [i] (212.02) [j]
	(280.00) [l]	(219.54) [l]		(222.67) [k]
$H^{12}C^{15}N$	263.18 [e]	202.00 [e]	205.23 [h]	202.18 [i] (200.15) [j]
$D^{12}C^{14}N$	210.73 [m] (209.36) [e]	181.23 [m] (180.05) [e]	181.47 [h]	181.45 [n] (179.67) [i] (177.51) [j]
	(213.91) [p]	(184.96) [p]		(186.88) [q]
$D^{12}C^{15}N$	200.69 [m] (199.33) [e]	171.46 [m] (170.30) [e]	171.60 [h]	171.62 [n] (169.85) [i] (167.79) [j] (169.58) [s]

Table 1. Extremal values and those calculated from D_e of q_e in MHz of some XYZ ($C_{\infty v}$) type molecules.

[a] This corresponds to B_e.
[b] This value of q_e is taken from Ref. [3].
[c] Value calculated from D_0 using the frequencies given in Ref. [3].
[d] This corresponds to q_{010}.
[e] This corresponds to B_0.
[f] Value calculated using D_0 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. [18].
[i] Calculated using B_0, D_e and ω_i (see Refs. [18, 19] for the experimental results).
[j] Calculated from B_0, D_0 and ω_i.
[k] Calculated from B_0, D_0 and ν_i; the anharmonic frequencies ν_i (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 ν_i.
[m] Computed from B_e and ω_i.
[n] Corresponds to B_e, D_e and ω_i.
[p] Determined using B_e and ν_i.
[q] Corresponds to B_e, D_e and ν_i.
[s] Estimated from B_e, D_0 and ω_i.

$(\zeta_{23}^{y})^2 = 0$. As seen from Eq. (4), this corresponds to $(q_e)_{min}$. Since, it is desirable to present the general relationship between q_e and D_e for this molecular type, we give the result here.

$$\text{i.e. } q_e = (2B_e^2/\omega_2)\,[1 + 4\omega_2^2(\omega_3^2 - \omega_2^2)^{-1} - 4\omega_1^2\omega_2^2\omega_3^2\,(\omega_1^2 - \omega_2^2)^{-1}\,(\omega_3^2 - \omega_2^2)^{-1}\,\{(D_e/4B_e^3) - (1/\omega_1^2)\}]\,. \quad (7)$$

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_vs for different excited states of the 'ω_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_{ri} is 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 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

$$\text{i.e. } \lambda_1^{(i)} + \lambda_3^{(i)} = G_{11}^{(i)} F_{11} + 2G_{13}^{(i)} F_{13} + G_{33}^{(i)} F_{33}\,;$$
$$\lambda_1^{(j)} + \lambda_3^{(j)} = G_{11}^{(j)} F_{11} + 2G_{13}^{(j)} F_{13} + G_{33}^{(j)} F_{33}\,. \quad (8)$$

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 l-doubling constant q_e can be used to derive a linear relation in the force constants (Σ^+). The l-doubling constant q_e is connected with the force constants through the relation [15]

$$\lambda_1(\zeta_{12}^{y})^2 + \lambda_3(\zeta_{23}^{y})^2 = F_{22}\lambda_2^{-1}[F_{11}(C_{12}^{y})^2 + 2F_{13}(C_{12}^{y})(C_{23}^{y}) + F_{33}(C_{23}^{y})^2] \quad (9)$$

[the zetas are connected with q_e through Equation (2)].

Discussion and Conclusion

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 ($C_{\infty v}$) 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 Σ^+ 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/ω_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 l-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_v in place of D_e (ii) B_0 or B_v in place of B_e and (iii) r_i in place of ω_i. Considering Eq. (7), one may write

$$q_e = a\,D_e + b \tag{10}$$

where

$$a = (-2/B_e\,\omega_2)\,\omega_1^2\,\omega_2^2\,\omega_3^2 \cdot (\omega_1^2 - \omega_2^2)^{-1}\,(\omega_3^2 - \omega_2^2)^{-1}$$

and

$$b = (2\,B_e^2/\omega_2)\,[1 + 4\,\omega_2^2(\omega_3^2 - \omega_2^2)^{-1} + 4\,\omega_2^2\,\omega_3^2\,(\omega_1^2 - \omega_2^2)^{-1}\,(\omega_3^2 - \omega_2^2)^{-1}]\,. \tag{11}$$

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

$$\Delta q_e/q_e = a\,(\Delta D_e)\,(a\,D_e + b)^{-1} = (\Delta D_e/D_e)\,(1 + b/a\,D_e)^{-1} \tag{12}$$

where Δq_e and ΔD_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 Δq_e is opposite to that of ΔD_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 rewritting Eq. (7) in the form

$$q_e = a'\,B_e^2 + b'/B_e \tag{13}$$

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

$$q_e + \Delta q_e = a'\,(B_e + \Delta B_e)^2 + b'[B_e^{-1}(1 + \Delta B_e/B_e)^{-1}] \tag{14}$$

or

$$q_e + \Delta q_e \approx a'\,B_e^2 + 2\,a'\,B_e\,\Delta B_e + b'[(1/B_e) - (\Delta B_e/B_e^2)]\,. \tag{15}$$

Hence, we get

$$\Delta q_e \approx [2\,a'\,B_e\,\Delta B_e - b'\,\Delta B_e/B_e^2]\,. \tag{16}$$

Equation (16) shows that Δq_e is positive if ΔB_e is positive. This, in other words, means that an increase in B_e causes an increase in the value of q_e. Since $B_e > B_v$ (including B_0), the use of B_v 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_v in place of D_e and B_v 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_v and B_v 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

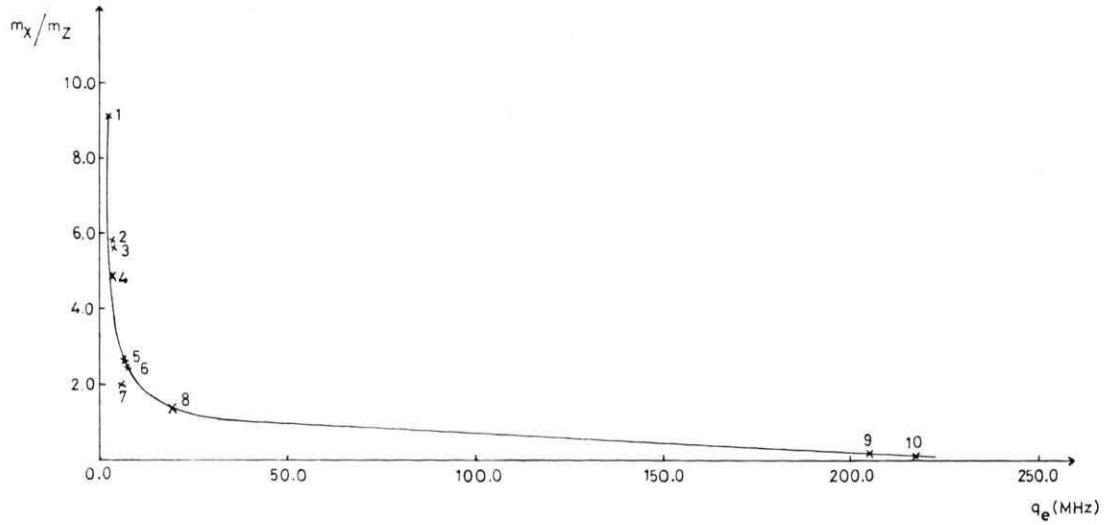

Fig. 1. q_e vs. the mass ratio (m_X/m_Z) for XYZ ($C_{\infty v}$) type molecules. 1. ICN, 2. ^{81}BrCN, 3. ^{79}BrCN, 4. SeCO, 5. ^{37}ClCN, 6. ^{35}ClCN, 7. ^{32}SCO, 8. FCN, 9. $H^{12}C^{15}N$, 10. $H^{12}C^{14}N$.

$(\omega_i - \nu_i)$ is small (e. g. non hydrides). In the case of HCN and DCN, however, the use of ν_i in place of ω_i leads to large deviations from the experimental results. In conclusion, it may be said that the above errors (due to the use of D_v, B_v and ν_i) do not in general exceed 5%, and hence one can employ D_v, B_v and ν_i (in cases where D_e, B_e and ω_i 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 ω_i are used in Eq. (7) to calculate q_e (c. f. the results for $D^{12}C^{14}N$ and $D^{12}C^{15}N$; 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_v) 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_d) type molecules) reported first by Cyvin et al. [20] and explained, later, theoretically by Müller et alias [21].

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