Bond Distance and the Rigid Rotor

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Molecules rotate about a center of mass. The parallel axis theorem

$$I = I_{cm} + Mr^2$$

can be employed, incorporating isotopomers to derive bond lengths. (Mr^2 is indicative of the extra energy required to rotate the body off-center)

There are three elementary bond distance constructs to consider, r_0, r_e and r_s . Additional constructions can be invoked, but I'll limit this discussion to these basics. r_0 , the effective bond distance, is found from ground state moments of inertia. r_e, the equilibrium bond distance, is found at the bottom of the internuclear potential governing vibrational motion in the Born-Oppenheimer approximation. [1] r_s , or substitution, is obtained from isotopomer data sets.

For the simplest case, the rigid rotator, one must procure r_0 using a minimum of two vibrational states. [2]

Usually the V_0 and V_1 vibrational levels are chosen as they are generally the easiest measured.

From p and q branch spacings and rotational quantum mechanics, whereby

$$E_j = BJ(J+1)$$

one can find the required moments of inertia. From the transition V_0 to V_1 the 2B rotational constant spacing is found. For the R branch

$$\Delta E = \nu_{vib} + 2B(J+1)$$

and for the P branch $\Delta E = \nu_{vib} - 2BJ$

m values, (where m = J" + 1 for the R branch and m = -J" for the P branch) are tabulated with corresponding frequencies, and after fitting a rotational constant B is obtained.

In the ideal case of a non-vibrating (or equilibrium) molecule, bond length is isotopically invariant, being solely determined by charge. [2]

Isotopic substitution will result in a change of the moment of inertia

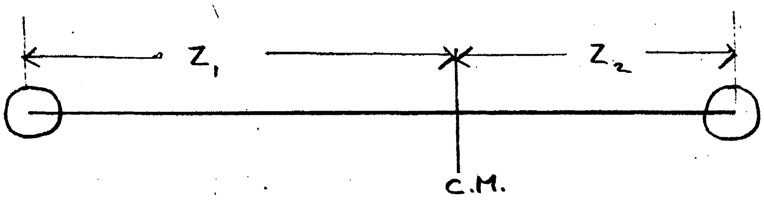
$$\mu' = \frac{M \Delta m}{M + \Delta m}$$

in direct correspondence to a less energetic branch line.

From the center of mass condition

$$m_1 z_1 + m_2 z_2 = 0$$

$$I' - I = (M' - M)\frac{M}{M'} z_2^2 \qquad (M = m_1 + m_2)$$

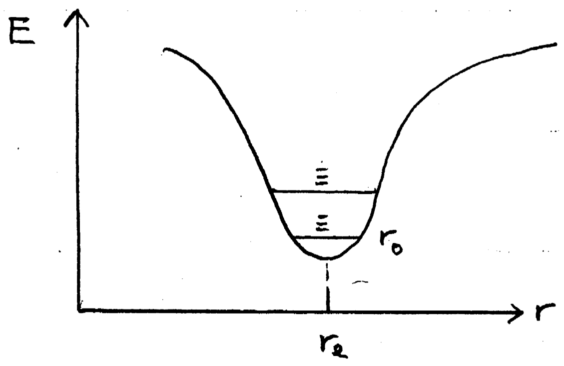


$$|z_2| = \left[\frac{(I' - I)}{M' - M}\,\frac{M'}{M}\right]^{1/2} \quad \text{or} \quad \left[\frac{\Delta I}{\Delta M}\,\frac{M'}{M}\right]^{1/2}$$

With the simplest case

$$r_v = \left[\frac{I}{\mu}\right]^{1/2} \qquad (\text{where } v = 0, e)$$

The r_s method requires one to obtain I_0 values for parent isotopomer and all other substituted daughter species. r_e is independent of isotopic specie, whereas r_0 is inside the potential energy curve and mass dependent. [3]



B_e is an unattainable state but can be approximated from

$$B_v = B_e - \alpha\left(v + \tfrac{1}{2}\right) \qquad (v = 0, 1, \ldots)$$

The later term, $\alpha\left(v + \frac{1}{2}\right)$, refers to the vibration-rotation constant. For this r_s method B_0 will be considered isotopically invariant.

The r_s recipe for a rigid rotor.

Tabulate: $\Delta I \; ; \; \Delta M \; ; \; M, M'$ for use in

$$|z_2| = \left[\frac{\Delta I}{\Delta M} \frac{M'}{M} \right]^{1/2}$$ and

calculate p, d_1, d_2 (parent, daughter isotopomers)

For instance

$$\left.\begin{array}{ll} p & {}^{1}H - {}^{79}Br \\ d_1 & {}^{1}H - {}^{81}Br \end{array}\right. \longrightarrow Z_{Br}$$

$$\left.\begin{array}{ll} d_1 & {}^{1}H - {}^{81}Br \\ d_2 & {}^{2}H - {}^{81}Br \end{array}\right. \longrightarrow Z_{H}$$

Then $|Z_H| + |Z_{Br}| = r_s$

Since it is assumed the atomic position do not change under substitution <u>one can literally graft the daughter isotopomer z distances back to the parent</u>.

The r_0 values for HBr

	B_0 (MHz)	I_0
$D^{79}Br$	127357.6334	$6.58932955 \cdot 10^{-47}\ Kgm^2$
$D^{81}Br$	127279.7639	$6.593360886 \cdot$
$H^{79}Br$	250360.12	$3.351977211 \cdot$
$H^{81}Br$	250282.75	$3.353013409 \cdot$

	ΔI
$H^{79}Br$ — $H^{81}Br$	$1.036198 \cdot 10^{-50}\ Kgm^2$
$D^{79}Br$ — $D^{81}Br$	$4.031338 \cdot$
$H^{79}Br$ — $D^{79}Br$	$3.23735234 \cdot 10^{-47}\ Kgm^2$
$H^{81}Br$ — $D^{81}Br$	3.24034748

	ΔM
$H^{79}Br$ — $H^{81}Br$	$3.3177223 \cdot 10^{-27}\ Kg$
$D^{79}Br$ — $D^{81}Br$	$3.3177223 \cdot$
$H^{79}Br$ — $D^{79}Br$	$1.6735539 \cdot$
$H^{81}Br$ — $D^{81}Br$	$1.6735539 \cdot$

M & M'

$D^{79}Br$	$1.348009286 \cdot 10^{-25}\ Kg$
$D^{81}Br$	$1.3812872 \cdot$
$H^{79}Br$	$1.32722186 \cdot$
$H^{81}Br$	$1.36447725 \cdot$

$$|z_2| = \left[\frac{\Delta I}{\Delta M}\,\frac{M'}{M}\right]^{1/2}$$

example:

p $H^{79}Br$
d_1 $H^{81}Br$

$$|Z_{Br}| = \left[\frac{1.036198 \cdot 10^{-50}\,Kg\,m^2}{3.3177223 \cdot 10^{-27}\,Kg}\;\frac{1.36447725 \cdot 10^{-25}\,Kg}{1.32722186 \cdot 10^{-25}\,Kg}\right]^{1/2}$$

$$|Z_{Br}| = 1.7919 \cdot 10^{-12}\ m$$

p. $H^{79}Br$
d_2 $D^{79}Br$

$$|Z_H| = \left[\frac{3.23735234 \cdot 10^{-47}\,Kg\,m^2}{1.6735539 \cdot 10^{-27}\,Kg}\;\frac{1.348009286}{1.32722186}\right]^{1/2}$$

$$|Z_H| = 1.4017 \cdot 10^{-10}\ m$$

		Parent
r_s	$= 1.4196 \cdot \underline{10^{-10}\ m}$	$H^{79}Br$
	$= 1.4175 \cdot$	$H^{81}Br$
	$1.4154 \cdot$	$D^{79}Br$
	$1.4174 \cdot$	$D^{81}Br$

$$r_0 = \left[\frac{I_0}{\mu}\right]^{1/2}$$

atom masses

$$H = 1.6653873 \cdot 10^{-27}\,Kg$$
$$D = 3.34449401$$
$$^{79}Br = 1.314295947 \cdot 10^{-25}\,Kg$$
$$^{81}Br = 1.343646318 \cdot 10^{-25}\,Kg$$

$$\mu_{H^{79}Br} = \frac{(1.6653873 \cdot 10^{-27}\,Kg)(1.314295947 \cdot 10^{-25}\,Kg)}{(1.6653873 \cdot 10^{-27}\,Kg + 1.314295947 \cdot 10^{-25}\,Kg)}$$

(example)

$$= 1.6653873 \cdot 10^{-27}\,Kg$$

$$r_0 = \frac{I_0}{\mu} = \left[\frac{3.351977211 \cdot 10^{-47}\,Kgm^2}{1.6653873 \cdot 10^{-27}\,Kg}\right]^{1/2}$$

$$r_0 = 1.4187 \cdot 10^{-10}\,m \quad H^{79}Br$$
$$1.42769 \cdot 10^{-10}\,m \quad H^{81}Br$$
$$1.42139 \cdot 10^{-10}\,m \quad D^{79}Br$$
$$1.42144 \cdot 10^{-10}\,m \quad D^{81}Br$$

Harmony has noted that it is necessary to use two B_v values (i.e, B_0 and B_1) to calculate B_e. [2, p. 12] For the diatomic

$$B_0 = B_e - \frac{\alpha_e}{2}$$

$$B_1 = B_e - \frac{3\alpha_e}{2}$$

Ignoring the higher order term one finds

$$I_e = \frac{h}{8\pi^2 B_e} \doteq I_0 = \frac{h}{8\pi^2 B_0}$$

For $D^{79}Br$ (example)

$$I_0 = \frac{6.62608 \cdot 10^{-34}\ J \cdot s}{8\pi^2 (127357.6334 \cdot 10^6 s^{-1})} =$$

$$= 6.589341 \cdot 10^{-47}\ Kgm^2$$

$$r_e = \left[\frac{(6.589341 \cdot 10^{-47}\ Kgm^2)}{\frac{(3.344357 \cdot 10^{-27} Kg)(1.3104705 \cdot 10^{-25} Kg)}{(3.344357 \cdot 10^{-27} Kg + 1.3104705 \cdot 10^{-25} Kg)}} \right]^{1/2}$$

$$= \left[\frac{6.589341 \cdot 10^{-47}\ Kgm^2}{3.261132 \cdot 10^{-27}\ Kg} \right]^{1/2}$$

$$r_e = 1.42147 \cdot 10^{-10}\ m$$

$(10^{-10} m)$	$D^{79}Br$	$D^{81}Br$
r_0	1.42147	1.42103
r_1	1.435689	1.43568

To estimate r_e from B_0 and B_1 one must take a mean. For $D^{79}Br$

$$r_e = \frac{1.42147 + 1.435689}{2} = 1.42858 \cdot 10^{-10} \text{ m}$$

and for $D^{81}Br$ $\quad r_e = 1.42835 \cdot 10^{-10} \text{ m}$

Tabulating all results

	$H^{79}Br$	$H^{81}Br$	$D^{79}Br$	$D^{81}Br$
r_0	1.4187	1.42769	1.42139	1.42144
r_s	1.4196	1.4175	1.4154	1.4174
$r_{e\ mean}$			1.4286	1.4284
$r_{e\,(2r_s - r_0)}$	1.4205	1.40731	1.40941	1.41336

Solving a simultaneous equation for $B_0 = B_e - \alpha_e$ and $B_1 = B_e = B_e - 3\alpha_e$ gives upon cancellation of α_e

$$\frac{3}{2} B_0 - \frac{1}{2} B_1 = B_e$$

Plugging in values for $D^{79}Br$ and $D^{81}Br$ gives for $D^{79}Br$

$$B_e = 1.2861299 \cdot 10^{11}.$$

$$r_e = \left[\frac{I_e}{\mu}\right]^{1/2} = \left[\frac{6.5250239 \cdot 10^{-47}\ Kg\,m^2}{3.2614985 \cdot 10^{-27}\ Kg}\right]^{1/2}$$

Then

$$D^{79}Br = 1.41443 \cdot 10^{-10}\ m$$
$$D^{81}Br = 1.41484 \cdot 10^{-10}\ m$$

Finding one set of values for α_e for both $D^{79}Br$ and $D^{81}Br$ I calculate

$D^{79}Br$ from B_0

$$127357.6334 \cdot 10^6/s + 1257 \cdot 10^6/s = B_e \quad [4]$$

from B_1 $\quad 1.286146334 \cdot 10^{11}$

$$r_e = \left[\frac{6.524940541 \cdot 10^{-47}\ Kg\,m^2}{3.26149853 \cdot 10^{-27}\ Kg}\right]^{1/2}$$

$$= 1.41442 \cdot 10^{-10}\ m$$

and for $D^{81}Br$

$$re = 1.41446 \cdot 10^{-10}\ m$$

Determining r_e by ignoring the higher term, or vibration-rotation interaction constant, is in many ways avoidance of the problem. Cancellation of the term, given B_0 and B_1 and simultaneously solving for B_e also brings into question just what exactly has been accomplished.

B_e by definition must account for any vibrational disruption of the rotational energies. The best approach would be to solve using an actual higher term which can be extrapolated from R branch compression and P branch rarefaction [6]. Comparing r_e (mean) and r_e ($2r_s$-r_0), as well as the 'simultaneous equation' method, doesn't shed too much light on the matter.

It is noted the later method, and the r_s method, are smaller valued than the effective method, or r_0 in this case. At least that is logical for deuterium. One would expect a minimum distance at equilibrium as well as inconsistent data with the hydrogen isotopomer.

References

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