

3.2.2 Symmetric top free radicals

3.2.2.1 Preliminary remarks

1 Introduction

At the time of the publication of the last supplement, symmetric top free radicals were something of a rarity. In the present edition, there are six such species which have been extensively studied and it seems appropriate to give them their own section.

As it happens, all of the molecules are in non-degenerate 2A_1 states; the effective Hamiltonian in this case is comparatively simple. It has been described by several authors (*e.g.* Herzberg [66Her], Brown [71Bro] and Hougen [80Hou]):

$$H = H_{\text{rot}} + H_{\text{cd}} + H_{\text{sr}} + H_{\text{srd}} + H_{\text{hfs}}.$$

The first term on the right hand side represents the rotational kinetic energy:

$$H_{\text{rot}} = A N_z^2 + B(N_x^2 + N_y^2) \quad \text{for a prolate symmetric top}$$

or

$$H_{\text{rot}} = C N_z^2 + B(N_x^2 + N_y^2) \quad \text{for an oblate symmetric top.}$$

The second term is the centrifugal distortion correction to the rotational kinetic energy:

$$H_{\text{cd}} = -D_N (N^2)^2 - D_{NK} N^2 N_z^2 - D_K N_z^4 \\ + H_N (N^2)^3 + H_{NK} (N^2)^2 N_z^2 + H_{KN} (N^2) N_z^4 + H_K N_z^6 + \dots$$

The next term in the effective Hamiltonian is the electron spin-rotation operator, written for a prolate symmetric top:

$$H_{\text{sr}} = \epsilon_{aa} N_z S_z + \frac{1}{2} \epsilon_{bb} (N_+ S_- + N_- S_+)$$

and the following one describes its centrifugal distortion corrections [79Bro]:

$$H_{\text{srd}} = D_N^S N^2 (N \cdot S) + \frac{1}{2} D_{NK}^S [N^2, N_z S_z]_+ + D_{KN}^S N_z^2 (N \cdot S) + D_K^S N_z^3 S_z$$

The final term, H_{hfs} , represents the nuclear hyperfine interaction. Its form for a C_{3v} molecule has been derived by Hougen [80Hou] and further discussed by Endo *et al.* [84End]:

$$H_{\text{hfs}} = \sum_i [a_{Li} \mathbf{L} \cdot \mathbf{I}_i + \sigma_i \mathbf{S} \cdot \mathbf{I}_i + \mathbf{S} \cdot \mathbf{T}_i \cdot \mathbf{I}_i],$$

where a_{Li} denotes the coupling constant between the orbital angular momentum and the i^{th} nuclear spin, σ_i is the Fermi contact parameter and \mathbf{T}_i is the dipole-dipole interaction tensor. For a C_{3v} molecule involving three equivalent nuclei, it is more convenient to take the following linear combinations rather than to use the individual nuclear spin angular momentum \mathbf{I}_i :

$$\mathbf{I}_0 = \mathbf{I}_1 + \mathbf{I}_2 + \mathbf{I}_3 \\ \mathbf{I}_{\pm} = \mathbf{I}_1 + e^{\pm 2\pi i/3} \mathbf{I}_2 + e^{\pm 4\pi i/3} \mathbf{I}_3.$$

and

Accordingly, the coupling constants are replaced by the linear combinations defined by

$$a_L = (a_{L1} + a_{L2} + a_{L3})/3,$$

$$\begin{aligned}\sigma_0 &= (\sigma_1 + \sigma_2 + \sigma_3)/3, \\ I_{\pm} &= (\sigma_1 + e^{\pm 2\pi i/3} \sigma_2 + e^{\pm 4\pi i/3} \sigma_3)/3, \\ T_0 &= (T_1 + T_2 + T_3)/3, \\ T_{\pm} &= (T_1 + e^{\pm 2\pi i/3} T_2 + e^{\pm 4\pi i/3} T_3)/3.\end{aligned}$$

and

The hyperfine Hamiltonian H_{hfs} can thus be rewritten as:

$$H_{\text{hfs}} = a_L \mathbf{L} \cdot \mathbf{I}_0 + \sum_{\alpha} [\sigma_{\alpha} \mathbf{S} \cdot \mathbf{I}_{-\alpha} + \mathbf{S} \cdot \mathbf{T}_{\alpha} \cdot \mathbf{I}_{-\alpha}],$$

where α sums over $+$, $-$ and 0 .

The matrix elements for the effective Hamiltonian have been given by Endo *et al.* for a doublet electronic state using a Hund's case (a) basis set [84End]. The basis set is $|L, A\rangle|v, l\rangle|S, \Sigma\rangle|J, P, M_J\rangle$ where the factors are, respectively, the electron orbital wavefunction, the (degenerate) vibrational wavefunction, the electron spin wavefunction and the rotational wavefunction. The quantum numbers A , l , Σ and P are associated with the z component of the orbital, vibrational, spin and rotational angular momenta (\mathbf{L} , \mathbf{G} , \mathbf{S} and \mathbf{J} , respectively).

2 List of tabulated parameters

A, B	rotational constants for a prolate symmetric top molecule
C, B	rotational constants for an oblate symmetric top molecule
D_N, D_{NK}, D_K	quartic centrifugal distortion parameters
H_N, H_{NK}, H_{KN}, H_K	sextic centrifugal distortion parameters
$\mathcal{E}_{aa}, \mathcal{E}_{bb}$	spin-rotational constants for a prolate symmetric top molecule
$\mathcal{E}_{cc}, \mathcal{E}_{bb}$	spin-rotational constants for an oblate symmetric top molecule
$D_N^S, D_{NK}^S, D_{KN}^S, D_K^S$	quartic centrifugal distortion corrections to the spin-rotation parameters
$a_F(\text{X})$	Fermi contact hyperfine parameter of nucleus X
$T_{aa}(\text{X}), T_{bb}(\text{X})$	Dipole-dipole hyperfine parameters of nucleus X for a prolate symmetric top molecule

3 Arrangement of molecules

1. SiF_3
2. MgCH_3
3. CaCH_3
4. SrCH_3
5. BaCH_3
6. CaOCH_3

4 References

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