

3.2.1 Linear polyatomic radicals

3.2.1.1 Preliminary remarks

1 Introduction

The rotational spectra of linear polyatomic molecules are very similar to those of diatomic molecules in the same electronic state. The reader is therefore referred to chapter 3.1 for additional information. Data are included here for molecules in $^2\Sigma$, $^3\Sigma$, and $^2\Pi$ states only. In the former two cases, the description of the energy levels is identical to that for the corresponding diatomic molecule (except that there are more vibrational modes). In the latter case, the situation is made more complicated by the interaction between electron orbital and vibrational angular momenta, known as the Renner-Teller effect [34Ren, 66Her]. For a triatomic molecule, the effect involves the bending vibration ν_2 and the coupling leads to a pattern of vibronic energy levels which have been described in many other places e.g. [66Her] and are labeled by the vibronic quantum number $K(= A + \ell)$ rather than the individual orbital and vibrational quantum numbers. There have been significant developments in the theoretical description of the vibronic energy levels over the past few years [80Jun, 82Bro] but the details of this work fall outside the scope of the present compilation.

The data reported for the molecules in the $^2\Sigma$, $^3\Sigma$, and $^2\Pi$ states have been analysed in terms of an effective Hamiltonian which refers to the rotational, spin and hyperfine levels of a particular vibronic state. The Hamiltonian is formulated in terms of the various angular momenta involved, namely, N , L , S , G , J , I , and F which are respectively the rotational, orbital, electron spin, vibrational, nuclear plus electronic, nuclear spin, and total angular momenta (strictly speaking, $N = R + L$ where R is the angular momentum of the nuclear framework). The effective Hamiltonian can be written

$$H_{\text{eff}} = H_{\text{rot}} + H_{\text{so}} + H_{\text{ss}} + H_{\text{sr}} + H_{\text{cd}} + H_{\text{LD}} + H_{\text{hfs}} + H_Q.$$

The terms on the right hand side refer to the rotational kinetic energy, the spin-orbit interaction, the spin-spin interaction, the spin-rotation interaction, centrifugal distortion effects, lambda-type doubling, the magnetic nuclear hyperfine interactions and the electric quadrupole coupling term. They have been described in detail elsewhere (see Section 3.1.5 and refs. [62Hou], [78Bro], [79Bro1]). Two alternative formulations can be found in the literature, one in terms of R^2 [70Hou] and the other in terms of N^2 [79Bro1]. The two approaches give identical results for a given data set except that the parameter values are slightly different. Interconversion between the two parameter sets is straightforward [87Bro]. For molecules in Π electronic states, subject to the Renner-Teller effect, special considerations may be required in treating the various terms in H_{eff} . Hougen has discussed the rotational Hamiltonian, H_{rot} , from this point of view [62Hou] and Russell and Beaudet have considered the magnetic hyperfine interactions [74Rus]. A general formulation of the lambda doubling terms has been given by Brown and Merer [79Bro2]:

$$H_{\text{LD}} = \frac{1}{2} o_v (S_+^2 + S_-^2) - \frac{1}{2} p_v (N_+ S_+ + N_- S_-) + \frac{1}{2} q_v (N_+^2 + N_-^2)$$

where o_v , p_v , and q_v are the lambda-doubling parameters for the vibrational level v , $S_{\pm} = S_x \pm iS_y$ and $N_{\pm} = N_x \pm iN_y$, and the operators are defined on the implicit understanding that they link the $A = 1$ and $A = -1$ components of the Π state only. The parameters can be related in turn to the electronic properties of the molecule.

The nuclear spin magnetic hyperfine interactions are represented by

$$H_{\text{hfs}} = a I_z L_z + b_F I \cdot S + \frac{1}{3} c (3 I_z S_z - I \cdot S) - \frac{1}{2} d (S_+ I_z + S_- I_z)$$

where a , b_F , c , and d are the four hyperfine parameters [52Fro, 78Bro] and the angular momentum operators are as defined above. The four terms describe the nuclear spin-orbit, the Fermi contact, the dipolar and the lambda doubling (dipolar) interactions respectively. Frosch and Foley [52Fro] originally

formulated the Hamiltonian in terms of a slightly different parameter b , dependent on both the Fermi contact and dipolar interactions:

$$b = b_F - \frac{1}{3} c.$$

In many cases, the parameter pair b and c is better determined by the data than b_F and c even though the latter might be considered to have more physical significance. For molecules in $^2\Sigma$ and $^3\Sigma$ states, the magnetic nuclear hyperfine effects can be described in terms of two parameters only, b_F and c (or b and c , if preferred). The magnetic hyperfine parameters give information on the spatial distribution of the open shell electrons [88Ste, 90Ama].

The nuclear electric quadrupole interactions are represented by

$$H_Q = \frac{eQq_0}{4I(2I-1)}(3I_z^2 - I^2) + \frac{eQq_2}{8I(2I-1)}(I_+^2 + I_-^2)$$

where eQ is the nuclear quadrupole moment and q_0 and q_2 are the electric field gradients parallel and perpendicular to the linear axis respectively [78 Bro]. The second term only shows a first order effect in Π states.

2 List of tabulated parameters

B	rotational constant for the molecule in a particular vibrational level. The subscript v has been omitted in the tables because the vibrational or vibronic states are indicated separately
D, H	centrifugal distortion constants for a given vibrational level
A	spin orbit coupling constant for a given vibrational level
A_D	centrifugal distortion to spin-orbit coupling
γ	spin rotation coupling constant for a given vibrational level
γ_D	centrifugal distortion to spin-rotation coupling
λ	electron spin dipolar coupling parameter for a given vibrational level
λ_D	centrifugal distortion of electron spin dipolar coupling parameter
o, p, q	lambda-type doubling parameters
o_D, p_D, q_D	
o_H, p_H, q_H	centrifugal distortion to lambda-type doubling parameters
a, b, c, d, b_F	nuclear spin magnetic hyperfine parameters
$h_{1/2}, h_{3/2}$ (or h_1, h_2)	combinations of magnetic hyperfine parameters in $^2\Pi$ states: $h_{1/2} = a + (b+c)/2$, $h_{3/2} = a - (b+c)/2$
eQq_0, eQq_2	nuclear electric quadrupole coupling constants ($\Delta I = 0$ and ± 2 terms respectively)
μ	electric dipole moment
ω_2	harmonic frequency for the bending vibration (ν_2)
q, q_N (or q_D)	ℓ – type doubling constant and centrifugal corrections in vibrationally excited degenerate states, see Vol. II/24A. Note that q is also in use for one of the lambda-type doubling parameters above
q_{NN} (or q_H)	
ε	Renner-Teller coupling parameter
$V_1^0, V_2^0, V_3^0, V_2^2$	coefficients in the intermolecular potential between OH and the Ar atom in the van der Waals' complex, Ar...OH

3 List of symbols used

$\tilde{X}^2\Sigma, \tilde{X}^2\Pi$	designation of $^2\Sigma$ or $^2\Pi$ electronic ground states
$^2\Pi, ^2\Delta, ^2\Phi$	designation of vibronic states with $ K = 1, 2$ or 3

v_1, v_2, v_3	vibrational quantum numbers for the three normal modes of a linear triatomic molecule Mode number 2 is always associated with the bending vibration
A	quantum number associated with component of orbital angular momentum L along internuclear axis
ℓ, Σ	corresponding quantum numbers for the components of the vibrational (G) and spin (S) angular momenta along internuclear axis
K	vibronic quantum number, valid in the presence of a strong Renner-Teller effect. Defined $K=A+\ell$
$\kappa(^2\Sigma), \mu(^2\Sigma)$	upper(κ) and lower(μ) vibronic $K=0$ sublevels in a $^2\Pi$ electronic state [62Hou]
e, f	designation of parity. States with parity $(-1)^{J-\frac{1}{2}}$ are labelled e , those with parity $-(-1)^{J-\frac{1}{2}}$ are labelled f [75Bro]
u, l	label for the upper and lower components of a parity doublet, in the situation where the parity is not known.

4 Arrangement of substances

1. C ₂ H	13. C ₁₄ H	25. HC ₆ N	37. SrOH
2. C ₃ H	14. CCN	26. HCCP	38. BaOH
3. C ₄ H	15. C ₃ N	27. HCCS	39. MgCN
4. C ₅ H	16. C ₅ N	28. HC ₃ S	40. MgNC
5. C ₆ H	17. CCO	29. HC ₄ S	41. CaNC
6. C ₇ H	18. C ₄ O	30. SiCN	42. MgC ₂ H
7. C ₈ H	19. C ₆ O	31. SiNC	43. CaC ₂ H
8. C ₉ H	20. C ₈ O	32. SiCCH	44. SrC ₂ H
9. C ₁₀ H	21. CCS	33. NaCH	45. ArOH
10. C ₁₁ H	22. C ₄ S	34. KCH	46. ArSH
11. C ₁₂ H	23. HCCN	35. MgOH	47. FeCO
12. C ₁₃ H	24. HC ₄ N	36. CaOH	

5 References

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