

3.2 Polyatomic radicals

3.2.0 Introduction

A radical is defined to be a molecule in an open shell electronic state. It is often, although not necessarily, very reactive and short-lived in a laboratory environment. Several new species have been studied since the publication of the previous supplement. Many of the new observations have been made by radio astronomers who now have access to frequencies up to 500 GHz. Experiments employing double resonance techniques (simultaneous irradiation with microwaves and either infrared or visible radiation) have also made a contribution to the development of the field. The information about linear molecules, in $^2\Sigma$, $^3\Sigma$, and $^2\Pi$ states, is contained in section 3.2.1. The non-linear radicals, almost all of which are triatomic, are presented in 3.2.2 (Symmetric molecules), 3.2.3 (Non-linear triatomic molecules), and 3.2.4 (Non-linear larger molecules).

Data which relate to molecular rotational energy levels have been fitted to the parameters of an appropriate effective Hamiltonian. Such a Hamiltonian must take account of all the many interactions which can arise for a molecule in a multiplet electronic state. The foundations for many of the features of this model have been securely laid by Van Vleck [51Van] with an important contribution for linear triatomic molecules in Π states (the Renner-Teller effect) having been made by Renner [34Ren]. There have been many subsequent papers dealing with different aspects of the effective Hamiltonian, some of which are listed in the previous supplement. For a good overall description, the reader is referred (still) to the third volume of Herzberg's book "Molecular Spectra and Molecular Structure" [66Her]. The effects of centrifugal distortion on the rotational energy levels, depending on their formulation, may cause indeterminacies among the parameters in the Hamiltonian. Watson [67Wat, 77Wat] has shown how these indeterminacies can be systemically removed. Watson's ideas about the expression of the effective Hamiltonian in terms of determinable parameters have been extended to the spin-rotation Hamiltonian and its centrifugal distortion corrections by Brown and Sears [79Bro]. A concise treatment of the various terms in the Hamiltonian, together with expressions for their matrix elements has been published by Hirota [85Hir].

Values for the inertial defect and the electric dipole moment quoted in this section have been recalculated where necessary using the currently accepted values for Planck's constant, Avogadro's number and the experimental value for the dipole moment μ of $^{16}\text{O}^{12}\text{C}^{32}\text{S}$. The first two of these are $h = 6.62606876(52) \cdot 10^{-34}$ Js and $N_A = 6.02214199(47) \cdot 10^{23} \text{ mol}^{-1}$ [99Moh]. The best determination of μ_{OCS} available to date is that by Lahaye, Vandenhoute and Fayt [86Lah] whose value is $0.7151887(26)\text{D}$. The value for the speed of light is now defined to be $c = 2.99792458 \cdot 10^8 \text{ ms}^{-1}$ [93Mi1]. The rotational constant times moment of inertia product on the ^{12}C basis is thus $B \cdot I = 5.05379006(65) 10^5 \text{ MHz amu } \text{\AA}^2 \equiv 16.8576291(22) \text{ amu } \text{\AA}^2 \text{ cm}^{-1}$.

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