

Landolt-Börnstein

Numerical Data and Functional Relationships in Science and Technology

New Series / Editor in Chief: W. Martienssen

Group II: Molecules and Radicals

Volume 24

Supplement to Volumes II/4, II/6, II/14, and II/19

Molecular Constants

**mostly from Microwave, Molecular Beam,
and Sub-Doppler Laser Spectroscopy**

Subvolume D

Constants for Radicals

Part 2

Polyatomic Free Radicals

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 Springer

ISSN 1615-1852 (Molecules and Radicals)

ISBN-10: 3-540-23112-9 Springer Berlin Heidelberg New York

ISBN-13: 978-3-540-23112-7 Springer Berlin Heidelberg New York

Library of Congress Cataloging in Publication Data

Zahlenwerte und Funktionen aus Naturwissenschaften und Technik, Neue Serie

Editor in Chief: W. Martienssen

Vol. II/24D2: Editor: W. Hüttner

At head of title: Landolt-Börnstein. Added t.p.: Numerical data and functional relationships in science and technology.

Tables chiefly in English.

Intended to supersede the Physikalisch-chemische Tabellen by H. Landolt and R. Börnstein of which the 6th ed. began publication in 1950 under title: Zahlenwerte und Funktionen aus Physik, Chemie, Astronomie, Geophysik und Technik.

Vols. published after v. 1 of group I have imprint: Berlin, New York, Springer-Verlag

Includes bibliographies.

1. Physics--Tables. 2. Chemistry--Tables. 3. Engineering--Tables.

I. Börnstein, R. (Richard), 1852-1913. II. Landolt, H. (Hans), 1831-1910.

III. Physikalisch-chemische Tabellen. IV. Title: Numerical data and functional relationships in science and technology.

QC61.23 .502'.12 62-53136

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Printed in Germany

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Cover layout: Erich Kirchner, Heidelberg

Typesetting: Authors and Redaktion Landolt-Börnstein, Darmstadt

Printing and Binding: AZ Druck, Kempten/Allgäu

SPIN: 11313410 63/3020 - 5 4 3 2 1 0 – Printed on acid-free paper

Preface

The present subvolume II/24D2 of volume II/24 *Molecular Constants mostly from Microwave, Molecular-Beam and Sub-Doppler Laser Spectroscopy* covers polyatomic free radicals. The literature up to and including the year 2000 is taken into account, starting from 1992/93. Previous data on paramagnetic species can be found in volumes II/4, II/6, II/14, and II/19.

The author presents the material in four chapters: Linear, Symmetric, Nonlinear Triatomic, and Larger Polyatomic free radicals. Each is headed by an introduction where the numerous intra-molecular interactions and their hamiltonians are extensively discussed and the coupling parameters are defined. The basic publications in the field are cited so the reader may use this compilation as a guide to spectroscopy of paramagnetic species.

Polyatomic paramagnetic molecules exist in a variety of electronic spin and electronic and vibrational angular momentum states, and they cannot be treated in terms of a standard hamiltonian like most of the diamagnetic species. The molecules in this sub-volume are therefore ordered according to their structural similarities, rather than following Hill's system as in the subvolumes II/24A, B, C. The author has included extensive listings of experimental frequencies. These will certainly be helpful to the user as predicting the rotational spectra of a free radical and their fine and hyperfine structures from a set of parameters must as yet be considered a cumbersome task.

The Zeeman effect needs some special attention here as the spin and orbital electronic g-factors are now redefined on the grounds of a recent agreement between quite a few spectroscopists and theoreticians [J.M. Brown et al., *Molec. Phys.* 98 (2000) 1597] on a change in their sign. The author has adopted this suggestion so that the spin and orbital electronic g-values are treated as negative quantities in this subvolume. The advantage of this usage is that it includes the electron in the general rule that the sign of a g-value determines whether the magnetic moment vector points parallel or anti parallel to the corresponding angular momentum. In this way, the electron has lost its exceptional status compared to nuclear or molecular rotational magnetism. Care must be taken with sign changes which may now be necessary in all equations containing electronic g-factors.

Thanks are due to the author for his competent work in a demanding, diverse field, and also to the editorial staff of Landolt-Börnstein, especially Dr. Christian Meier, for completing this handsome issue.

Ulm, May 2005

The Editor

Editor

W. Hüttner

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