MOLECULAR SPECTRA
and
MOLECULAR STRUCTURE

IV. CONSTANTS OF DIATOMIC MOLECULES

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Since the publication in 1950 of Vol. I, Spectra of Diatomic Molecules of Molecular Spectra and Molecular Structure, much progress has been made in the field. While there have been some important refinements in the theory of diatomic molecular spectra, most of the advances have been in the further exploration of individual spectra. Not only has the number of molecules about which some spectroscopic data are available been increased by a factor of 2 to 3, but also the spectroscopic information about the molecules known in 1950 has been vastly extended. This is due to the observation of new electronic states (about three times as many as known before), the enormous improvements in the accuracy of the constants of the states known in 1950, and the determination of higher order constants.

In view of the increasing use of spectroscopic information on diatomic molecules in other fields of physics, in chemistry, and in astrophysics, it appeared desirable to prepare an up-to-date version of the table of molecular constants in the appendix of Vol. I. This updating proved to be far more time-consuming than originally anticipated, and it is only now, 10 years after its initiation, that we are able to present such a table, which, instead of the original 80 pages (plus 30 pages of bibliography), now fills a volume of 700 pages.

In the interest of economy, and unlike the original version, the new table has been produced by photo-offset from the final manuscript. Thus, typographical errors, which would have been likely to occur in such a difficult typesetting job, were entirely eliminated. We have spared no effort to make the table as up-to-date as possible. The date of final revision of each part is indicated. While the principal constants of each state of each molecule are listed uniformly in the body of the table, additional constants that could not be fitted in are given in the footnotes. Also, many qualifications and other explanations are added in this way.

We hope that users of these tables will find them helpful in supplying up-to-date constants as well as references to the most recent literature.

We are greatly indebted to many colleagues who have supplied advance
information on recent unpublished work. The tables edited by the late B. Rosen were of great help to us in finding some of the earlier literature on many of the molecules dealt with therein. We have also greatly profited by the special tables prepared by P. H. Kruценie on O₂ and CO and by Kruzenie and A. Lofthus on N₂. But wherever possible we have checked with the original publications. Particularly valuable to us throughout the entire course of this work were the Berkeley Newsletters prepared by J. G. Phillips and S. P. Davis; without them, a great many of the publications listed in the tables and in the appendix might have escaped our attention.

Although the final manuscript was prepared by one of us (K.P.H.), many drafts of the tables were typed by M. P. Thompson, and much checking of numbers and references was done by her and I. Dabrowski. We are most grateful for their efforts.

Finally, we must acknowledge that the National Research Council of Canada supported this work throughout the protracted period of its preparation by permitting one of us to spend all of his time for more than 10 years—and the other, part of his time—on this project and by providing other necessary facilities.

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INTRODUCTION

In this volume, we present a compilation of available data for all diatomic molecules and ions. The format of most of the tables follows closely that used in Table 39 of Volume I of this series; that is, the various known electronic states and their symmetry symbols appear in the first column, and in the adjacent columns the electronic energy (Tₑ), the vibrational constants (ωₑ and ωᵥₑ), the rotational constants (Bₑ, Aₑ, Dₑ), and the internuclear distance (rₑ) are given. In the last three columns, the observed transitions involving the particular electronic state, their ν₀ values, and the references on which the information is based are listed. The columns “ωᵥₑ” and “Remarks” of the previous table have been omitted, but this information is given in the footnotes. In addition, in the footnotes, references about Franck-Condon factors, potential functions, and other constants are given such as the following:

A Spin-orbit interaction parameter  
λ Spin-spin interaction parameter  
γ Spin-rotation interaction parameter (not to be confused with the rotation-vibration interaction constant, γᵥ)  
τ Radiative lifetime  
f Oscillator strength (f value)  
μₑ Electric dipole moment in Debye units (1 D = 10⁻¹⁸ esu cm).  
gₑ Rotational g factor in units of nuclear magnetons (μₑ)  
Δ-type doubling constants p, q, . . .  
Hyperfine structure (hfs) constants such as the magnetic coupling constants, a, b, c, d, and the electric quadruple coupling constant, eqQ.

At the top of each table, the reduced mass μ of the molecule is given, as well as the dissociation energy Δₑ₀ in the ground state and the ionization potential (I.P.). Dissociation energies for states other than the ground state are easily derived if the dissociation products are known. Normally they are not listed explicitly.

The notation for spectra of diatomic molecules has been standardized for many years. We have followed this notation throughout this volume. There is one important change in the notation, which was internationally agreed upon after the publication of Volume I: the change from K to N for the angular momentum excluding electron spin and the corresponding quantum number. There are still authors who are not aware of this change, which was agreed upon because, in polyatomic molecules, K represents the component of J in the direction of the top axis, and both K and N are needed there when S $\neq 0$.

All numbers in the tables are in cm$^{-1}$ units except where otherwise indicated. The conversion factors and fundamental constants which we have used are based on "The 1973 Least-Squares Adjustment of the Fundamental Constants" by Cohen and Taylor (J. Phys. Chem. Ref. Data 2 [4], 663-734 [1973]). The most important of these are the following:

1 eV = 8065.479 cm$^{-1}$
1 kcal/mol = 349.755 cm$^{-1}$
1 kj/mol = 83.5935 cm$^{-1}$
c = 2.99792458 X 10$^{10}$ cm s$^{-1}$
$m^{(12)} = 1.6605655 \times 10^{-24}$ g
$h \overline{8\pi c} = 27.9932 \times 10^{-40}$ g cm$^{-2}$ cm$^{-1}$
k = 16.8576 a.m.u. Å$^{-2}$ cm$^{-1}$
$\hbar c = 0.695030 K^{-1}$ cm$^{-1}$
1 K = 0.000086173 eV

The reduced masses are referred to $m^{(12)} = 12.0000000$ and are calculated from the atomic masses given in the table by Wapstra and Gove (Nucl. Data Tables 9, 265-301 [1971]).

All the data in the tables have been reviewed critically. They are, however, presented without error limits. The addition of meaningful and uniformly evaluated error limits would have meant an enormous increase in the time required to complete these tables. Instead, we hope that the number of digits quoted may serve as a very rough indication of the estimated order of magnitude of the error, generally ±9 units of the last decimal place. Where the last digit is given as a subscript, we expect that the uncertainty may considerably exceed ±10 units of that last decimal place.

In almost all cases, and unless stated otherwise, the constants $\omega_0$, $\omega_1$, $\omega_2$, $B_0$, $\alpha_0$, and $D_0$, that are listed are effective constants; that is, apart from sign they correspond to the coefficients $Y_{kn}$ in the Dunham series expansion for the term values

$$T_{kn} = \sum_{lm} Y_{kn}(\nu + l)^{\frac{3}{2}}T_{lm}(J + 1)^{m}$$

The molecules are listed in strict alphabetical order (e.g., BaBr, BaCl precede BrB and BrCl, even though this separates the latter from Br$_2$). Positive and negative ions, in this order, follow immediately after the corresponding neutral molecule. Constants for hydrides, deuterides, and tritides are given separately; for all other molecules, they are given for only one, usually the most abundant, isotope or for the natural isotopic mixture. In the latter case, the mass number for the most abundant species of one or both of the constituent atoms appears in parentheses and the reduced mass $\mu$, also in parentheses, has been calculated accordingly.$^6$

As in Volume I, the footnotes are referred to by lower-case letters*$^a$*$^b$... continuing where necessary with *$^c$*$^d$... in tables that extend over several pages, the sequence of footnotes starts with *$^a$ on each page.

The references to the original literature are numbered in chronological order for each molecule and follow immediately at the end of the corresponding table. In order to save space, they are given in abbreviated form, omitting the initials of the authors and using code names for the journals as well as for the monographs. An alphabetical list of these abbreviated publication titles may be found on pages 1 through 7.

Each table carries the date (month and year) of its last revision. Considering the inevitable delay between publication of a paper and its eventual digestion for the purpose of the table, we estimate that the information in the table can be regarded as complete up to an effective cutoff time of three or four months prior to the indicated date. When the date is followed by the letter A, it indicates that in the appendix on pages 690 through 716 a list and short description may be found of additional publications that came to our notice after completion of the particular table.

$^6$For ions with unequal nuclear charges, the reduced mass is not given explicitly. An ambiguity arises here with respect to the calculation of $\mu$, which we did not undertake to resolve; instead, we used the reduced mass of the corresponding neutral molecule for the evaluation of internuclear distances. This approximation will normally not significantly increase the uncertainty of the result.
The signs are defined as follows:

\[ G(v) = \omega(v + \frac{1}{2}) - \omega_{2}(v + \frac{1}{2})^2 + \omega_{4}(v + \frac{1}{2})^4 \]
\[ + \omega_{6}(v + \frac{1}{2})^6 + \ldots \]

\[ F_{J}(J) = B_{J}(J + 1) - D_{J}(J + 1)^2 + H_{J}(J + 1)^3 \ldots \]

\[ B_{v} = B_{v} - \alpha_{v}(v + \frac{1}{2}) + \gamma_{v}(v + \frac{1}{2})^2 + \ldots \]
\[ D_{v} = D_{v} + \beta_{v}(v + \frac{1}{2}) + \ldots \]

The higher order constants are given in the footnotes.

\( T_{v} \) is usually calculated from the observed transitions without taking into account the quantity \( Y_{o0} \) in the upper or lower state. Exceptions are mentioned in the footnotes.

The dissociation energy \( D_{v}^{0} \) is always defined as the energy of the ground state atomic products relative to the lowest existing level of the molecule. In almost all cases, there is a footnote after \( D_{v}^{0} \), which explains the method used in its derivation. The description “thermochemical value” is used to indicate any determination (mass spectrometric, flame photometric, or other) that involves the evaluation of a thermochemical equilibrium. Where necessary, thermochemical values that have been derived from exchange reactions have been adjusted to take account of recent changes in the dissociation energies of the reference molecules.

In agreement with common practice, the first ionization potential (in eV) is taken as the energy difference of the lowest existing level of the ion and the lowest existing level of the neutral system. Analogous definitions apply to positive as well as negative ions although for the latter, the I.P. is more commonly referred to as electron affinity of the neutral. Higher ionization potentials have in some cases been added in the table or in the footnotes. Electron impact appearance potentials have only rarely been included since their accuracy is usually low (typically \( \pm 0.5 \) eV).

It appears nearly impossible to give a generally applicable definition of the band origins. Here, origins in singlet systems normally refer to the zero lines; that is, they include the \( J \) independent term \( -BA_{J} \), which some authors prefer to include in the rotational energy expression. Similarly, for case “a” multiplet states, a corresponding definition applies to individual sub-bands; exceptions to these rules are usually indicated in the footnotes. For intermediate coupling or coupling close to case “b”, we frequently refer to the zero-point of the Hill-Van Vleck (or equivalent) expression; an explanation is usually given in the footnotes. Multiplets very close to case “b” are often treated as singlets disregarding electron spin. In all cases where our definition of the origin deviates strongly from that used by the original author, we have indicated this in the accompanying footnote.

The magnitude and sign of the \( \Lambda \)-type doubling is indicated in many instances in footnotes by quoting either the difference \( B(R,P) - B(Q) \), which is equivalent to \( B(\Pi) - B(\Pi) \) for transitions involving a \( \Sigma^{+} \) state, or the leading terms in the expression giving the observed splitting as a function of \( J \). For the labeling of the parity doublet levels, we have adopted the recommendations of Brown et al. (J. Mol. Spectrosc. 55, 500 [1975]):

\[ \begin{align*}
\text{integral } J: & \quad e \text{ levels have parity } (+1)^{J} \\
\text{half-integral } J: & \quad f \text{ levels have parity } (-1)^{J} \\
\end{align*} \]

The sign of the splitting is defined by

\[ \Delta \nu_{\alpha}(J) = F_{\alpha}(J) - F_{\alpha}(J) = -\Delta \nu_{\alpha}(J) \]

For some case “\( b^{2} \) II states we give \( \Delta \nu_{\alpha}(N) \) and refer to the \( F_{\alpha} \) component.

The following symbols are used throughout the table:

- H: Data obtained from band head measurements
- Z: Data obtained from, or referring to, band origins
- R: Shaded towards longer wavelengths
- V: Shaded towards shorter wavelengths
- (): Uncertain data
- [ ]: Data refer to \( v = 0 \) or lowest observed level. \( T_{v} \) values in square brackets give the energy of this level relative to the minimum of the ground-state potential energy curve. Vibrational frequencies in square brackets correspond to \( \Delta G(0) \) or the lowest observed integral.

\( \{ \} \): Hypothetical levels
- \( \rightarrow \): Emission
- \( \leftarrow \): Absorption

According to international agreement the upper state always comes first.

* Indicates a reference number where a good record or reproduction of the spectrum may be found.