

1 Introduction

1.1 General remarks

The II/28 volume contains data on the geometric parameters (internuclear distances, bond angles, dihedral angles of internal rotation, *etc.*) of free polyatomic molecules including free radicals and molecular ions. (For the diatomic structures measured by high-resolution spectroscopy, see [1], and for molecular structures in crystals, see [2]. For the structures of free molecules published before 1960, see [3].) Earlier volumes of the present series for polyatomic structures were published as II/7, 15, 21 and 23 [4–7]. They cover the data between 1960 and 1993. A revised version of these volumes, which also includes data from 1994 and 1995, was published as II/25 [8–11].

This volume is made of four subvolumes, each containing the geometric parameters determined in the gas phase either by an analysis of the rotational constants (and sometimes the vibrational constants) obtained from microwave, infrared, Raman, electronic and photoelectron spectroscopy or by an analysis of electron diffraction intensities. Most of the structures listed in the tables are for molecules in the electronic ground state, but structures for electronically excited states have also been included as far as they are available (see [Sect. 1.5](#)).

In this fourth subvolume, II/28D, the structures of molecules containing five or more carbon atoms are listed. These data have been taken from the literature published between January 1996 and December 2002; a few structures published after 2002 are also included. They are linked to the data from II/25D subvolume [11] by cross-references. The II/25D subvolume presents all the reliable data for the molecules with five or more carbon atoms published between 1960 and 1995; some structures published before January 1960 are also included.

As a general principle, the structures reported in the original literature have been taken after critical reexamination. With few exceptions, those molecules for which geometric parameters were reported only qualitatively, *e.g.*, when only equilibrium molecular symmetry was reported, have been omitted. The policy governing the selection of data and the assessment of their uncertainties differs slightly according to experimental method, as described in detail below. For molecules studied by more than one experimental technique, *e.g.*, by microwave and infrared spectroscopy or by microwave spectroscopy and electron diffraction, a decision has been made in each case as to whether it is necessary or desirable to list more than one geometric structure. When spectroscopic and diffraction structures are listed together for the purpose of critical comparison, they are in general regarded as compatible with each other, to the best of our present knowledge, within their experimental uncertainties; otherwise, specific comments are given in each case. (Note that a slight difference exists in the physical significance of the structural parameters reported in spectroscopy and electron diffraction: see [Sect. 1.3](#).)

1.2 Experimental methods

1.2.1 Spectroscopy

Molecular spectroscopy extends from the radiofrequency region down to the soft X-ray region. The rotational spectra of molecules, which normally appear in the microwave and far-infrared regions, provide rotational constants and related parameters. These experimental data have been used for more than half a century as the major spectroscopic sources of reliable geometric structures of free molecules, which are summarized in the present volume. The target of studies has been extended in recent years to the geometric structures of weakly bound molecular complexes in the gas phase by the development of experimental and theoretical techniques.

The vibrational spectra appear in the infrared region and the electronic spectra in the visible and shorter-wavelength regions, although there exist a number of exceptions. In long-wavelength regions, microwave and far-infrared, the resolution is inherently high, so that the rotational constants are readily determined with high precision. In the infrared, visible and ultraviolet regions large grating spectrographs were set up to resolve the rotational structures of molecules. However, recent developments of spectroscopic techniques, in particular the introduction of lasers and development of Fourier transform spectroscopy, have changed the situation in these regions considerably. In the infrared, some fixed-frequency lasers such as the carbon dioxide and nitrous oxide lasers have been combined with external electric or magnetic fields to bring molecular transitions into resonance with laser frequencies; the electric-field case is referred to as laser Stark spectroscopy and the magnetic-field case as laser magnetic resonance or LMR. LMR was originally developed in the far-infrared region. More recently, infrared spectroscopy with tunable laser sources has become more common. Diode lasers are available in nearly the entire infrared region and also, in recent years, from the near infrared to the visible region; the color center laser oscillates in the region 1.5...3.5 μm ; and a difference frequency output can be generated in the 2...4.2 μm region by nonlinear mixing of two visible lasers, one tunable and the other fixed in frequency. Recent development of nonlinear devices has extended the longest wavelength to 10 μm or even longer. In the visible and shorter wavelength regions grating spectrographs have been traditionally employed; however, dye lasers are now widely used, and harmonic generation of the output or nonlinear mixing of two or more outputs allows us to cover the wavelength region down to the vacuum ultraviolet. Laser spectroscopy has improved not only the resolution, but also the sensitivity so that even a few molecules prepared in the form of a beam have been detected, eliminating the Doppler broadening from their spectra. Many complexes formed by weak intermolecular forces have also been detected in beams. The recent development of Fourier spectroscopy is remarkable; spectrometers of high performance are now commercially available and allow us to record the spectra of molecules from 10 cm^{-1} to $5\times 10^4\text{ cm}^{-1}$ (200 nm) with Doppler-limited resolution over most of this range. The method of Fourier transformation has also been introduced in microwave spectroscopy in combination with free jet expansion of the sample and has resulted in much improvement in resolution and sensitivity.

Considerable improvements have recently occurred in infrared spectroscopic instrumentation. For high resolution studies, grating instruments have been replaced by Fourier transform spectrometers which are capable of resolving 0.002 cm^{-1} or better and have precision of measurement of $1\times 10^{-4}\text{ cm}^{-1}$ (3 MHz) or even $5\times 10^{-5}\text{ cm}^{-1}$, the accuracy being dependent on calibration lines, typically $4\times 10^{-4}\text{ cm}^{-1}$. A joint effort by many laboratories is aimed at providing a coherent set of calibration lines so that accuracies near $1\times 10^{-4}\text{ cm}^{-1}$ can be reached in most spectral regions. Recommendations to correct previous wavenumber standards have been issued by the International Union of Pure and Applied Chemistry (IUPAC) [12].

Diode laser and difference-frequency laser spectrometers have also been developed with instrumental resolution high enough that the Doppler width of the lines in the spectrum sets the practical limit to resolution. These spectrometers can achieve high precision in wavenumber measurements, but the accuracy is again highly dependent on calibration lines. Since molecular jets are becoming more common nowadays, Doppler widths can be reduced, making laser techniques more promising. At present, Raman measurements for structural purposes are still made in the visible region of the spectrum using grating spectrometers and tend to be roughly 10 to 100 times less precise than infrared measurements.

In recent years, new schemes have been introduced in Raman studies, taking advantage of Fourier transform spectrometers and of lasers. For instance CARS techniques can now achieve nominal resolutions of 0.003 to 0.005 cm^{-1} with accuracies of 0.001 cm^{-1} or better. Unfortunately, these experiments are still limited to a small number of skilled laboratories. Nevertheless, joint works using both IR and Raman data are appearing, Raman being especially useful for infrared inactive bands.

Both infrared and Raman studies have an advantage over microwave spectroscopy in that a much larger number of lines can be conveniently measured, often at higher values of the rotational quantum numbers. Many papers now combine IR and microwave data to derive a full set of rotational constants.

In modern papers ground-state constants are frequently reported with cited uncertainties $\pm 1\times 10^{-7}\text{ cm}^{-1}$ (3 kHz) from infrared work and $\pm 1\times 10^{-5}\text{ cm}^{-1}$ (0.3 MHz) from Raman studies. In band spectra, two sets of rotational constants are obtained, those of the upper and lower states involved in the transition, and a statistical treatment allows the differences between the constants to be determined to precisions approach-

ing or equal to microwave uncertainties (1 kHz or less). Thus equilibrium rotational constants of polar molecules can be quite precisely calculated by using microwave-determined B_0 constants and infrared-determined α constants. If the values of some of these α constants are missing, they can be substituted by reliable *ab initio* values. Despite the recent instrumental improvements, the resolution available from both infrared and Raman studies is still much lower than that from microwave spectroscopy, and therefore, studies are limited to fairly small and simple molecules. However, these techniques are not restricted to polar molecules as is the case for microwave spectroscopy, and thus infrared and Raman spectroscopy play an important role in the determination of the structures of small symmetric non-polar molecules.

Many early infrared and Raman papers have reported studies on polar molecules that subsequently have been reexamined in the microwave region. In most of these cases, the microwave work is clearly superior and the infrared results have not been included in these tables. In some cases, however, the addition of even relatively low-precision optical data, when combined with microwave data, will lead to improved structural estimates. For example, frequently the A_0 (or C_0) rotational constant of a symmetric top can be obtained either from perturbation-induced transitions in the infrared spectrum or from suitable combinations of transitions in a fundamental band, a combination band and a hot band, or else by the analysis of a perpendicular band in the Raman spectrum. It is not possible to obtain this rotational constant in the pure rotational spectrum of a symmetric top molecule, and therefore combining the optical and microwave data leads to a high improvement in determining the positions of the off-axis atoms of such molecules.

These spectroscopic methods with high resolution provide us with *rotational constants*, from which we may extract information on the geometric structures of molecules. The rotational constants are inversely proportional to the principal moments of inertia. In a rigid molecule, the three principal moments of inertia (two for a linear molecule) are defined such that

$$I_a \leq I_b \leq I_c, \quad (1)$$

where a , b and c denote the three principal axes of inertia. The rotational constants are given by

$$A = h/8\pi^2 I_a, \quad B = h/8\pi^2 I_b, \quad C = h/8\pi^2 I_c \quad (A \geq B \geq C), \quad (2)$$

where h denotes Planck's constant. A *linear* molecule has two identical rotational constants, I_a being taken to be zero. A *spherical top* has three identical rotational constants. They are usually denoted by B . Therefore, only one piece of information on molecular geometry can be obtained for the two types of molecules per isotopic species. The definition of a *symmetric top* is that two of the three rotational constants are equal; $A > B = C$ for a prolate symmetric top, and $A = B > C$ for an oblate symmetric top. In these cases, at most two independent constants can be determined; usually only the B rotational constant is obtained from pure rotational spectra because of the selection rules. An *asymmetric top* molecule in general gives three independent rotational constants, but for a rigid, planar molecule the relation $I_c = I_a + I_b$ holds, and only two of the three are independent. The *inertial defect*, defined as $\Delta = I_c - I_a - I_b$, has a small and, in most ordinary cases, positive value for many planar molecules and is accounted for mainly by vibration-rotation interactions, as discussed below. For most molecules the number of independent geometric parameters exceeds that of the available independent rotational constants. Therefore, in order to determine the geometric parameters completely one has to work with isotopically substituted species as well.

The geometric significance of the rotational constants is somewhat obscured by the contributions of intramolecular motions. In most quasi-rigid molecules, because the frequencies of vibration are high compared with those of rotation, the rotational constants observed correspond to the inverse moments of inertia averaged over the vibrational amplitudes. Averaging is in general quite complicated. When all the intramolecular vibrations have small amplitudes and there are no accidental degeneracies or resonances, the rotational constants, for example the B constant, in the v -th vibrational state are given by expressions of the form

$$B_v = B_e - \sum_s \alpha_s^B (v_s + d_s / 2) + \dots, \quad (3)$$

where v_s and d_s denote the vibrational quantum number and the degeneracy of the s -th normal mode, respectively. Accordingly even for the ground vibrational state the rotational constant B_0 is not identical with the *equilibrium rotational constant* B_e , which can be interpreted purely geometrically by Eq. (2), namely,

$$B_e = h / 8\pi^2 I_b^{(e)}. \quad (4)$$

The *vibration-rotation constants* α_s^B are complicated functions of the harmonic (quadratic) and anharmonic (mainly cubic) potential constants [13] and depend on the masses of the component atoms. Since a rotational constant is inversely proportional to a moment of inertia, α_s^B does not simply represent averaged vibrational contributions. It has, however, been proven [14] that the rotational constant corrected for the harmonic part of α_s^B gives the moment of inertia which corresponds to the real vibrational average.

The corrected rotational constant is often denoted as B_z , *i.e.*,

$$B_z = B_0 + \sum_s \alpha_s^B (\text{harmonic}) d_s / 2 = h / 8\pi^2 I_b^{(z)}. \quad (5)$$

When a semi-rigid molecule has one or more intramolecular motions of large amplitude such as internal rotation, inversion and ring puckering, it is much more difficult to interpret the rotational constants. However, by treating such large-amplitude motions separately from small-amplitude vibrations, one can often calculate from the observed spectra the effective rotational constant, which may then be analyzed as if there were only small-amplitude vibrations. In weakly bound complexes such as van der Waals complexes, component molecules execute labile motions with each other, so that it is fairly difficult to determine the geometric parameters. Even for such molecules we may determine the symmetries of the complexes at equilibrium, although the deviations from the equilibrium geometry can be quite large. In the following tables we add a comment "large-amplitude motion" and list "effective symmetry class", for molecules like complexes which execute large-amplitude motions.

The vibration-rotation spectra and/or the rotational spectra in excited vibrational states provide the α_s^B constants and, when all the α_s^B constants are determined, the equilibrium rotational constants can be obtained by extrapolation. This method has often been hampered by anharmonic or harmonic resonance interactions in excited vibrational states, such as Fermi resonances arising from cubic and higher anharmonic force constants in the vibrational potential, or by Coriolis resonances. Equilibrium rotational constants have so far been determined only for a limited number of simple molecules. To be even more precise, one has further to consider the contributions of electrons to the moments of inertia, and to correct for the small effects of centrifugal distortion which arise from transformation of the original Hamiltonian to eliminate indeterminacy terms [15]. Higher-order time-independent effects such as the breakdown of the Born-Oppenheimer separation between the electronic and nuclear motions have been discussed so far only for diatomic molecules [16].

Often the spectroscopic methods can show the presence of symmetry elements in a molecule without going into a detailed numerical analysis of the rotational constants. Because the spectrum of a symmetric top appears regular, it is easy to show that the molecule has a C_n axis with $n \geq 3$. The statistical weight due to degeneracy of nuclear spins can supply additional information. Even for an asymmetric top a C_2 axis causes intensity alternations in its spectrum. A plane of symmetry can be detected by isotopic substitution of one of two atoms located symmetrically with respect to the plane. For a molecule of the form H_2M where the two hydrogen atoms are symmetrically placed with respect to the symmetry plane, we will have only one singly-deuterated species, HDM. In cases where a C_{3v} symmetric internal rotor like the methyl group is attached to the framework such that one C–H bond is in a symmetry plane, we will have two kinds of singly-deuterated species: one species with the C–D bond in the symmetry plane and the other out of the plane, the latter having the statistical weight of two. If the internal rotation barrier is low, the energy levels of the latter species may be split into two by the tunneling. A small inertial defect suggests that a molecule is planar or very nearly planar at equilibrium.

1.2.2 Electron diffraction

The design of a gas electron diffraction apparatus is similar to that of an electron microscope, but the electron optical system is much simpler. The sample gas is introduced into the diffraction chamber through a nozzle, and the electrons scattered by the sample molecules near the nozzle tip are either collected on a photographic plate or measured directly by electron counting. Typical experimental conditions are as follows: electron accelerating voltage, ≈ 50 kV, corresponding to electron wavelength ≈ 0.05 Å; electron beam diameter, ≈ 0.1 mm; nozzle diameter, ≈ 0.3 mm; nozzle-to-detector distance, $\approx 20\text{--}60$ cm; sample pressure at the nozzle tip, about a few Torr. For a sample having a much lower vapor pressure at room temperature, the sample is heated during the experiment.

Since the scattering intensity decreases very rapidly with the scattering angle, a rotating sector, which has an opening proportional to the cube of the radius, is used for photographic measurements to compensate for the rapidly falling intensity. Equivalent filtering methods are used with other types of electron detectors. The photographic density (usually ranging from about 0.2 to 0.8) is measured by a microphotometer. The photographic density is converted to electron intensity by use of a calibration function. Most of the electron diffraction data listed in the following tables have been obtained by this sector-microphotometer method. Several structures obtained by non-photographic measurements of electrons scattered from short-lived transient chemical species by laser excitation are also included in the tables.

The intensity I_T is a function of the scattering variable,

$$s = (4\pi/\lambda) \sin(\theta/2), \quad (6)$$

where λ is the electron wavelength and θ is the scattering angle. When a smooth background,

$$I_B = I_{\text{atomic}} + I_{\text{inelastic}} + I_{\text{extraneous}}, \quad (7)$$

is subtracted from I_T , the molecular term,

$$I_M = I_T - I_B = \sum_{i \neq j} |f_i| |f_j| \cos(\eta_i - \eta_j) \exp(-\frac{1}{2} l_{ij}^2 s^2) \sin s(r_{ij} - \kappa_{ij} s^2) / s r_{ij} \quad (8)$$

is obtained. The molecular term is a sum of contributions from all the atom pairs $i - j$ in the molecule. The experimental process of gas electron diffraction is to measure and analyze I_M in order to derive the internuclear distance r_a and the root-mean-square amplitudes l (sometimes denoted as u), often abbreviated as "the mean amplitude". The complex atomic scattering factor,

$$f(s) = |f(s)| \exp[i\eta(s)], \quad (9)$$

is usually calculated with sufficient accuracy by use of an atomic potential function. The mean amplitudes can also be calculated if the quadratic force field of the molecule is known. The asymmetry parameter κ represents a slight (often negligible) deviation of the argument from a linear function of s . The significance of the r_a distance is described in [Sect. 1.3.2](#).

The molecular term I_M , or sometimes I_M/I_B , is analyzed by a least-squares method, and the bond distances, the bond angles (and other geometric parameters such as the dihedral angles of internal rotation and the angles related to ring geometry) or the nonbonded distances, and some of the mean amplitudes are determined. The rest of the mean amplitudes are usually constrained to either calculated or assumed values. The ratio, $(I_M/I_B)_{\text{obs}}/(I_M/I_B)_{\text{calc}}$, is often determined in the analysis as another empirical parameter. Whether this ratio, often called the index of resolution, is close to or appreciably less than unity is a good indicator of the quality of the experiment. However, the mean amplitudes and the index of resolution are not listed in the following tables, because they have no direct geometric consequence. The number of adjustable parameters depends on the accuracy of the experimental intensity and on the complexity of the molecule. The analysis often requires assumptions about molecular symmetry and/or the parametric values on which the molecular term depends only weakly. In studies of conformational and other equilibria, differences in the "frame" structures of component species are often assumed to be equal to those estimated according to results of quantum chemical calculations, or simply ignored. The uncertainties origi-

nating from these assumptions, if significant, are included in the error estimates of the final parameter values (see [Sect. 1.4.3](#)).

In comparison with other methods for determining molecular geometry, such as spectroscopy (see [Sect. 1.2.1](#)) and X-ray crystallography, the merits of gas electron diffraction are the following:

- 1) The average values of internuclear distances (particularly bond distances) in free molecules can be determined directly and, in many cases, accurately.
- 2) In principle, the only restrictions on the sample molecule are a sufficient vapor pressure and chemical stability. Polar or nonpolar, light or heavy, small or large molecules can be studied.

On the other hand, conventional electron diffraction has the following drawbacks:

- 1) Only the distance parameters averaged in thermal equilibrium, instead of those in individual quantum states, can be obtained. Therefore, the parameters derived from electron diffraction are subject to various vibrational effects. These effects can be considerable in nonrigid ionic molecules present in the vapors of salts at high temperatures.
- 2) An accurate measurement of the molecular term needs much caution. Any undetected accident in the experiment or analysis can cause serious, often undiscovered, systematic error in the geometric parameters derived.
- 3) The resolution of internuclear distances is limited by thermal vibration to only about 0.1 Å and cannot be improved experimentally except in special cases, such as PF₃, when nonbonded distances allow a resolution. Closely spaced, inequivalent distances are measured only as their weighted average values, their differences remaining very uncertain.
- 4) When the molecule under study contains elements of very different atomic numbers, the parameters relating to lighter atoms may be very uncertain. As a result of 3) and 4), in the worst cases even qualitative conclusions derived from electron diffraction on molecular geometry (such as the structural formula, equilibrium symmetry and the presence of conformers) can be in error.
- 5) Besides the above errors, the distance parameters may be systematically uncertain by as much as a few parts per thousand. The source of this error is in the scale factor (the electron wavelength times the nozzle-to-detector distance).

1.2.3 Combined use of electron diffraction and spectroscopy, theoretical calculations, or other methods

The disadvantages of electron diffraction mentioned above can be appreciably reduced if data obtained from other methods of structure determination are used conjointly. Vibrational spectroscopy supplies information on the force field, which is used very frequently in analyses of ED data for the calculation of mean amplitudes, shrinkage corrections, *etc.* (see [Sect. 1.3.2](#)). The equilibrium molecular symmetry determined by spectroscopy may be assumed, and the rotational constants determined by high-resolution spectroscopy may be used to adjust the scale factor and to set constraints on the geometric parameters. In principle, the structure can thus be determined with less ambiguity and more accuracy than either by spectroscopy or by electron diffraction alone [17]. Many examples are listed in the following tables, *e.g.*, electron diffraction plus microwave spectroscopy, abbreviated as ED, MW. For this purpose, the experimental data derived from different methods should be analyzed in terms of a consistent set of geometric parameters, usually in terms of the r_z parameters described in [Sect. 1.3.1](#), so as not to introduce additional systematic error. See general references [E-9], [E-24] for details.

The geometric structure and the force field estimated by quantum chemical (*ab initio* and density functional theory (DFT)) calculations [18] are often taken into the analysis as valuable sources of information [19, 20]. Molecular-mechanics calculations [21] were also widely used in the past [20]. Many examples of the joint use of these theoretical structural data are given in the following tables.

Differences between related geometrical parameters are very often (especially in the conformational analysis) assumed at the values from quantum chemical calculations, as in the MOCED (Molecular Orbital Constrained Electron Diffraction) method [19]. Method of flexible restraints, SARACEN (Structure

Analysis Restrained by *Ab initio* Calculations for Electron diffraction), proposed by Rankin and his group [22], are also used to overcome the limitations of ED analysis [22–24].

Combined use of experimental data and results of quantum chemical calculations demands to use the structural parameters of the same type. They could be equilibrium parameters, which are results of quantum chemical calculations. There are two alternative schemes to obtain equilibrium structure from ED data. The first one is based on the conventional r_a/r_g distances routinely derived at an initial stage of ED analysis with subsequent conversion of these parameters into r_e distances by incorporating appropriate harmonic and anharmonic vibrational corrections. This scheme was developed by Morino, Bartell, Kuchitsu and their coworkers [25–29]. Recent developments by Sipachev [30, 31] are also used within similar scheme. The second scheme was established by Spiridonov and coworkers [E-25], [E-42]. In this procedure, the equilibrium distances and the second (and higher-order) derivatives of the potential energy function taken at the minimum position (force constants) are refined simultaneously from ED data if the solution of the vibrational problem is available. The force constants can also be taken from quantum chemical calculations after appropriate scaling. Since the shape of the potential energy function can be important for adequate description of molecular dynamics, the used potential energy function (harmonic, anharmonic, *etc.*) and coordinates (rectilinear, curvilinear) are mentioned in the comment or footnote to the table.

Sometimes an NMR spectrum of molecules dissolved in a liquid crystal provides information on the geometric structure [32], which can also be taken into the analysis of electron diffraction data [33]. Mass spectrometry is also used with electron diffraction for estimating the composition of the sample vapor [34]. See also [E-43] for recent examples.

1.3 Significance of geometric parameters

The internuclear distances and angles listed in the following tables are based on various different definitions. Some of them are defined on physical and geometrical principles, while others are defined operationally, *i.e.*, by the method used for deriving the parameters from the experimental data. Numerically, the differences may not necessarily be important in comparison with experimental uncertainties, but it is always important to specify the definition of the parameters determined in order to make a precise and systematic comparison of experimental structures with one another or with the corresponding theoretical structures, such as those derived from quantum chemical (*ab initio* and density functional theory) calculations. A brief summary of the definitions is made in the present section. For a more detailed discussion of the significance of the structures and their relationship, see General References [E-10], [E-20].

1.3.1 Spectroscopy

In most spectroscopic studies, nuclear positions in the molecule-fixed coordinates are directly derived from the rotational constants, and bond distances and angles are then calculated from the nuclear coordinates. This may be contrasted with the electron diffraction case, where internuclear distances are first derived from experiment, and angles or nuclear coordinates are calculated from the internuclear distances (see [Sect. 1.3.2](#)). The equilibrium (r_e) and average (r_{av} or r_z) structures, which have well-defined physical significance, are reported occasionally, but most other cases quote the r_0 or r_s structures operationally derived from spectroscopic experiments.

(a) r_0 structure: A set of parameters obtained from the zero-point ("ground state"¹⁾) rotational constants is called the r_0 structure. Sometimes the rotational constants of a sufficient number of isotopic species are combined. In other cases, assumptions are made for some of the parameters. As pointed out in [Sect. 1.2.1](#), the ground-state rotational constants do not correspond to the moments of inertia averaged

¹⁾ "ground state" can and often does also mean ground electronic state.

over the ground vibrational state, but rather their inverses. It is therefore difficult to assess the exact physical meaning of the r_0 parameters. Furthermore, the r_0 parameters derived from different combinations of isotopic species are often widely different from one another. For example, $r_0(\text{C-H})$ distances can show deviations of as much as 0.1 Å. Note also that the relation $I_c = I_a + I_b$ for a planar molecule does not strictly hold for the ground-state rotational constants and this introduces supplementary ambiguities. This remark also applies to the r_s structure, below.

(b) r_s structure: As demonstrated by Costain [35], a set of geometric parameters that are much more consistent than the r_0 parameters can be obtained when only isotopic differences of rotational constants are used. Such a structure is called a substitution (r_s) structure. Kraitchman's equations [36] are used most conveniently for calculating the r_s structure. For a linear molecule the coordinate of the i -th atom a_i is given by

$$a_i^2 = \Delta I_b / \mu, \quad (10)$$

where ΔI_b is the *change* in the moment of inertia upon substitution of the i -th atom by its isotope. When the isotopic atom has a mass differing from the original atom by Δm_i , μ is given by $M\Delta m_i/(M+\Delta m_i)$, where M is the total mass of the parent molecule.

For a general asymmetric top, Kraitchman gave the following equation:

$$a_i^2 = \frac{\Delta P_a}{\mu} \left[1 - \Delta P_b / (P_a - P_b) \right] \left[1 - \Delta P_c / (P_a - P_c) \right]. \quad (11)$$

Equations for b_i^2 and c_i^2 are obtained by cyclic permutation of a , b and c . The moment P_a is defined by

$$P_a = (-I_a + I_b + I_c)/2, \quad (12)$$

P_b and P_c being defined in a similar way, and ΔP denotes the change of P on isotopic substitution. When a molecule has a plane or axis of symmetry, the corresponding equations are simpler.

All the singly substituted isotopic species are needed to obtain a complete r_s structure. However, this is sometimes impossible, *e.g.*, when the molecule contains atoms having only one stable nuclide such as ^{19}F , ^{31}P , ^{127}I , or difficult, *e.g.*, for a chemical reason, to make complete isotopic substitutions. In these cases, one is forced to use a first-moment equation or a condition that the cross-products of inertia be zero. In some cases even a part or all of the three moments of inertia of the parent species are used. The r_s structure thus obtained is in reality a hybrid of the r_s and r_0 structures. Nevertheless, even in these cases the structure is usually called r_s .

In the r_s scheme the coordinates of an atom located far from a principal inertial plane can be determined accurately, whereas those of an atom located close to an inertial plane are poorly defined, irrespective of the atomic mass. In the latter case the relative signs of the coordinates are difficult to determine, because Kraitchman's equations give only the absolute values. For small coordinates, doubly-substituted species may be of some use [37].

It has been shown for diatomic molecules that the r_s parameter is a simple average of the r_0 and r_e parameters. This relation holds only approximately, or may even fail, for polyatomic molecules. However, Watson [38] demonstrated that, if higher-order terms were neglected in the expansion of moments of inertia in terms of the isotope mass difference, the equilibrium moment of inertia was approximately given by $2I_s - I_0$, where I_s denoted the moment of inertia calculated using r_s coordinates.

(c) r_{av} (r_z) structure: When a set of the B_z constants defined in Eq. (5) is used instead of B_0 , the average structure in the ground vibrational state is obtained. This structure is usually called r_{av} or r_z [14, 39]. The r_z structure primarily defines the average nuclear positions during the vibrational motion, as remarked above. Hence, the $r_z(\text{X-Y})$ distance between the nuclei X and Y defines the distance between the average nuclear positions instead of the average of the instantaneous X-Y distance. A simple calculation shows that for a molecule with small vibrational amplitudes

$$r_z \cong r_e + \langle \Delta z \rangle_0, \quad (13)$$

where Δz denotes the instantaneous displacement, Δr , of $r(\text{X}-\text{Y})$ projected on the equilibrium $\text{X}-\text{Y}$ axis (taken as a temporary z axis), and 0 denotes the average over the ground vibrational state. Because of the presence of nuclear vibrations perpendicular to this z axis, r_z does *not* agree with the real average $\text{X}-\text{Y}$ distance $r_e + \langle \Delta r \rangle_0$. In general, it is not easy to estimate the difference between r_z and r_e , *i.e.*, $\langle \Delta z \rangle_0$, even for a bond distance. On the other hand, the difference between $\langle \Delta r \rangle$ and $\langle \Delta z \rangle$ can be estimated with sufficient accuracy by the use of the quadratic force field. The average bond angle can be defined unambiguously in terms of the average nuclear positions.

The r_z nuclear position depends on the mass of the nucleus. Therefore, the isotope effect must be known precisely when the B_z constants of other isotopic species are needed for a complete determination of the r_z structure. The r_z structure from such isotopic substitution is highly sensitive to the estimated (or assumed) isotope effect on r_z positions. This presents a serious difficulty in the experimental derivation of the r_z structures for all but the simplest molecules [40, 41].

The r_z structure can be generalized to excited vibrational states. The average nuclear positions for a vibrational state, characterized by a set of vibrational quantum numbers ν may be defined in a similar way.

(d) $r_e(r_m)$ structure: When all the α_s^A , α_s^B and α_s^C constants given in Eq. (3) have been determined, the equilibrium constants A_e , B_e and C_e are obtained. If a sufficient number of these constants are available, the equilibrium (r_e) structure, which defines the nuclear positions corresponding to the potential-energy minimum, can be determined. For a few simple molecules the α constants are given as functions of a limited number of third-order anharmonic potential constants which are common to all isotopic species. Therefore, if a number of rotational constants is determined for isotopic species in the ground as well as excited vibrational states, these anharmonic potential constants may be determined simultaneously with the r_e structural parameters [42]. The geometric significance of A_e , B_e and C_e (Eq. (4)) and r_e is unambiguous. However, because of the various experimental difficulties, accurate r_e structures are currently known for only a small number of simple molecules, as listed in the following tables.

In view of this situation, Watson [38] proposed what he called an r_m structure. As mentioned above, he pointed out that $2I_s - I_0$, which he referred to as I_m , was very close to the equilibrium moment of inertia I_e . Watson called the structure derived from a set of I_m the "mass-dependence" (r_m) structure. In a number of examples, he has shown that the r_m structure is indeed very close to the r_e structure, except for some parameters involving hydrogen. A drawback of this method is that data for more isotopic species than are necessary for the r_s method are needed for structure determination. Nakata *et al.* [43–45] pointed out that there exist additivity relations for isotopic effects on the structure parameters and employed this fact to eliminate higher-order terms in the expansion of moments of inertia in terms of isotope mass differences which were neglected in the original treatment of Watson. In this way Nakata *et al.* have expanded the applicability of the r_m method. A similar approach was proposed by Harmony *et al.* [46–48]. They noted that the ratio $\rho = I_s/I_0$ is not significantly isotope-dependent (but may be different for different inertial axes) and proposed to use $[I_m^p]_i = (2\rho - 1)[I_0]_i$ for the moment of inertia of the i -th isotopic species. The structure thus obtained is called the r_m^p structure.

Another effective structure, denoted as the r_{1e} structure, is also used by certain MW groups. This structure is based upon the equation, $I_0 = I_{\text{rigid}}(r_{1e}) + \varepsilon$, where I_0 and $I_{\text{rigid}}(r_{1e})$ denote the ground-state moment of inertia and the moment of inertia calculated from the r_{1e} coordinates, respectively, under the assumption that ε is independent of isotopic species [49].

A comment is given on the structural parameters of molecular complexes reported by a few groups. They regarded, for example, the distance between the centers of mass of the two components of a complex as an r_s parameter, because they thought that the complex was formed by "substituting" one component molecule to a place near the second component molecule, *i.e.*, by "isotopic" substitution. However, such parameters are listed in the present compilation as r_0 , since this interpretation is certainly not in conformity with the widely accepted convention of r_s .

1.3.2 Electron diffraction

An average internuclear distance can be regarded as the first moment of the probability distribution function of this distance, $P(r)$, which is approximately Gaussian unless the distance depends strongly on a large-amplitude vibration [25].

(a) r_a distances: When the asymmetry parameter κ in Eq. (8) is small, the distance parameter derived directly from an experiment of electron diffraction is r_a . This parameter is exactly equal to the center of gravity of the $P(r)/r$ distribution [26, 28],

$$r_a = r_g(1) \equiv \left(\int P(r) dr \right) / \left[\int (P(r)/r) dr \right]. \quad (14)$$

(b) r_g distances: If the $P(r)$ function is approximately Gaussian, then r_a is related to the center of gravity of $P(r)$, r_g , as

$$r_g = r_g(0) \equiv \left[\int r P(r) dr \right] / \left[\int P(r) dr \right] \cong r_a + l^2 / r_a, \quad (15)$$

where l is the mean amplitude. In contrast with the r_z defined in Eq. (13), the $r_g(X-Y)$ bond distance is a *real* (instead of *projected*) average, over thermal equilibrium, of the instantaneous X–Y distance, namely,

$$r_g = r_e + \langle \Delta r \rangle_T. \quad (16)$$

The r_e bond distance can be estimated if the bond-stretching anharmonicity is assumed. For example, for a group of similar bonds (*e.g.*, for the C–C bonds in hydrocarbons), the average displacements $\langle \Delta r \rangle_T$ are estimated to be nearly equal to one another, so that the observed differences in the r_g distances may well be approximated as those in the r_e distances. For this reason, many of the recent studies of electron diffraction report the r_g bond distances together with the r_a distances derived directly from experiment.

On the other hand, a set of the r_g bond distances and nonbonded distances cannot define a physically meaningful bond angle without corrections for linear or nonlinear "shrinkage effects" arising from the curvilinear path followed by atoms during a vibration [50]. The angle parameters determined by electron diffraction, either from the r_a distances or from the r_g distances, are quoted in the following tables as effective angles, when no corrections for the shrinkage effects have been made. The effective angles derived from the r_a distances are denoted as θ_a . The difference between an effective angle and the well-defined angles, such as the θ_e or θ_z angles derived from the r_e and r_z structures, respectively, depends on the amplitudes of bending, puckering, or torsional vibrations. This difference can often be estimated with sufficient approximation, since the shrinkage effect can be calculated if the quadratic force field of the molecule is known.

(c) r_e distances: The r_e bond distance can be estimated from r_g if the anharmonicity is known. In several recent studies (see, for example, [51]) anharmonicity has been estimated using scaled anharmonic force field from quantum chemical calculations. In a few cases (for small molecules), anharmonicity can be estimated directly from ED intensities on the basis of an assumed potential energy function model (see, for example, [E-25], [52–54]).

(d) r_α and r_α^0 structures: A lot of electron diffraction studies report the θ_α angles defined in terms of a set of the r_α (bonded and nonbonded) internuclear distances derived [55] from the corresponding r_g distances by

$$r_\alpha = r_g - \left(\langle \Delta x^2 \rangle_T + \langle \Delta y^2 \rangle_T \right) / 2r - \delta r, \quad (17)$$

where Δx and Δy denote the displacements perpendicular to the equilibrium nuclear axis (z) and δr denotes a small displacement due to centrifugal force. The shrinkage effects are eliminated in this structure.

The r_α distance corresponds to the distance between the thermal-average nuclear positions,

$$r_\alpha \cong r_e + \langle \Delta z \rangle_T \quad (18)$$

and when it is extrapolated to zero Kelvin temperature,

$$r_\alpha^0 = \lim_{T \rightarrow 0} r_\alpha \cong r_e + \langle \Delta z \rangle_0 \quad (19)$$

the r_α^0 structure is practically identical with the r_z structure. For a joint analysis of electron diffraction and spectroscopy discussed in [Sect. 1.2.3](#), the r_a or r_g distances observed by electron diffraction should be converted to the r_α^0 distances in order to make a consistent analysis for the r_z nuclear positions. In practice, the extrapolation from r_α to r_α^0 can be approximated on the basis of simple assumptions about anharmonicity. Except in a large-amplitude case, the uncertainty due to the r_α to r_α^0 conversion can be regarded as trivial.

1.3.3 Table of distance parameters and their definitions ^{a)}

Symbol	Definition
r_e	Distance between equilibrium nuclear positions
r_{av}, r_z, r_α^0	Distance between average nuclear positions (ground vibrational state)
r_α	Distance between average nuclear positions (thermal equilibrium)
r_0	Distance between effective nuclear positions derived from rotational constants of zero-point vibrational levels
r_s	Distance between effective nuclear positions derived from isotopic differences in rotational constants
r_m	Distance between effective nuclear positions derived from the mass-dependence method of Watson, very close to r_e for molecules without hydrogen atoms. r_m^p is the distance obtained by a slightly modified method of Harmony <i>et al.</i>
r_{le}	Distance related to the effective structure derived from isotopic moments of inertia after isotope-independent correction ε
r_g	Thermal average value of internuclear distance
r_a	Constant argument in the molecular term, Eq. (8), equal to the center of gravity of the $P(r)/r$ distribution function for specified temperature (no correction for the shrinkage effects usually being made)

^{a)} Some authors distinguish between "mean value" and "average value". However, the two words are used interchangeably in the following tables.

1.4 Uncertainties

1.4.1 Microwave spectroscopy

In many cases, authors give uncertainties originating only from the experimental errors in the rotational constants. Since microwave spectroscopy gives rotational constants with six to eight significant digits, this source of error is very small in comparison with other systematic errors. In the r_s scheme, error estimates often rely on the consistency of the results when more than the necessary number of isotopic species are available. These estimates include some of the uncertainties due to vibration-rotation interactions, but probably not all.

In the following tables, an attempt has been made to list either the r_e or the r_z structures, because they are physically well-defined as mentioned in [Sect. 1.3](#). In a few cases where the r_e structures are reported, bond distances have been determined to a few parts in 10^4 . Higher-order effects are of this order of magnitude or less. For the r_z structure, the systematic error due to the B_0 to B_z conversion may contribute to the total uncertainties, which are roughly a few parts in 10^3 or less. On the other hand, when different isotopic species are combined, the above-mentioned isotope effect on the nuclear positions may cause errors in r_z distances of 0.01 Å or more.

Most recent microwave papers report r_s structures with judicious estimates of errors. Although the contributions of vibration-rotation interactions are taken into account only empirically in most of these cases, errors given in the original papers are reproduced in the tables. However, in cases where the number of isotopic species investigated is small or the vibration-rotation interactions are apparently not considered properly, errors are slightly increased and indicated accordingly.

Generally speaking, smaller errors are assigned to the r_s parameters than to the r_0 parameters because of the consistency of the data. For the r_0 parameters, errors given in the original papers have been increased in most cases. Reported errors have also been increased in cases where some of the parameters are assumed because of the shortage of experimental data. In these cases the assumed parameters are mentioned in the tables. Curl [56] has developed a least-squares method, called the diagnostic least squares, by which the uncertainties in the "assumed" parameters may be taken into account. By this method, more parameters than the number of input experimental data can be "determined". The results depend obviously on authors' estimates of the uncertainties in the "assumed" parameters. In these cases errors listed in the tables have been made somewhat larger than the original estimates.

In summary, the uncertainties represent the "reasonable limits of error" estimated by E. Hirota. In other words, the true parameter is expected to be in the range of the errors listed in the tables except under very unusual circumstances.

1.4.2 Infrared and Raman spectroscopy

Bond distances obtained in infrared and Raman studies are normally r_0 or r_e distances. Although data from the infrared are now, in general, precise enough to obtain r_s distances, the large amounts of pure rare isotopic species required to obtain these data preclude the substitution technique, and only a handful of partial r_s structures have been obtained by optical methods. In these tables, whenever both r_e and r_0 structures have been derived for a given molecule, only the r_e structure is listed. Uncertainties in r_e parameters are not easily estimated since for polyatomic molecules the study of several vibration-rotation bands is required and quite often the used data come from several different laboratories and have been obtained over a period of years. The derivation of r_e parameters also often necessitates certain assumptions regarding the effects of perturbations, especially Fermi resonances. The limitations of r_0 parameters have been detailed above in [Sect. 1.3.1](#).

In the following tables the uncertainties given for the infrared and Raman-derived structures are those cited by the authors. In a few cases where the errors appear to be overly optimistic, a footnote is inserted to this effect. The structural parameters of a few molecules have been computed using rotational con-

stants reported in the literature, and the errors cited are based on the experimental uncertainties and the effects of errors of model.

1.4.3 Electron diffraction

Purely random errors in the geometric parameters determined by electron diffraction are usually estimated in a least-squares analysis from differences between the observed and calculated intensities. However, the errors in the geometric parameters are by no means distributed randomly, and the following systematic errors often make much more important contributions.

(a) Experimental sources: Systematic errors in the measurement of I_M (see [Sect. 1.2.2](#)) are one of the most significant sources of error. Inaccurate sector calibration and nonuniform extraneous scattering are typical examples. An error in the scale factor increases or decreases all the distances in the same proportion, while the angles remain undisturbed. Systematic errors may be even larger under unfavorable experimental conditions, for example, when the experiment is done at very high temperature, when the sample is unstable and/or impure, or when only a small quantity of sample is available.

(b) Analytical sources: The estimation of the background (I_B in Eq. (7)) and various assumptions made in the analysis are other important sources of systematic error. In particular, the uncertainty in the difference between nearly equal, inequivalent internuclear distances depends so delicately on various sources of error that it is very difficult to estimate. These distances correlate strongly with mean amplitudes; when mean amplitudes are fixed at assumed values in a least-squares analysis, the systematic error in the distances caused by this correlation is sometimes overlooked. The uncertainty in angle parameters derived with neglect of shrinkage corrections (see [Sect. 1.3.2](#)) is also difficult to estimate, particularly when the system has a large-amplitude vibration. Where a slight deviation from linearity or planarity is indicated by an analysis which neglects shrinkage corrections or which does not explicitly take into account large-amplitude motions, the deviation may be spurious; in such a case an explicit remark is made to this effect.

The standard errors estimated in a least-squares analysis can be used as a measure of relative precision, *i.e.*, to decide which parameters in the molecule under study can be determined more precisely than others. Nevertheless, their absolute magnitudes are always underestimated, since the essential parts of the systematic errors mentioned above are dissolved by adjustment of variable parameters and therefore overlooked. Such systematic errors can be discovered and corrected only by a critical examination of measurements on a sample of precisely known structure made under analogous experimental conditions or by a comparison of the rotational constants calculated by use of the parameters obtained by electron diffraction with those determined by spectroscopy. Such a test has not always been made in the past, however. Even when the test is made, it never provides complete assurance that the data are free from all the systematic errors.

Thus many authors estimate total experimental uncertainties not only from the random standard errors obtained in their least-squares analyses but also from the systematic errors estimated somehow from their past experience, although their methods may differ appreciably from laboratory to laboratory. Accordingly, the uncertainties estimated in the following tables generally include *all* the supposedly possible systematic errors, *i.e.*, estimated *total* errors rather than only *random* errors, unless indicated otherwise.

The styles of representation of the uncertainties also differ widely from laboratory to laboratory. Estimated standard deviations (e.s.d.) are often multiplied by a certain constant (2, 2.6 or 3). Several authors report "estimated limits of error" when they regard the probability of finding the geometric parameters *outside* the range as *negligible*. In general, the tables follow the styles reported by the authors and in each case define the meaning of the listed uncertainty, since it is considered to be inappropriate, if possible at all, to alter them into a uniform style.

In a few cases, the uncertainties have been re-estimated, and explicit remarks to this effect have then been made. Sometimes attention is drawn to a potential source of significant systematic error, such as the presence of sample impurity, implicit assumptions in the analysis such as the neglect of significant

shrinkage effects, or strong correlation among the parameters. For some of the geometric parameters reported in the original papers, only their weighted average values are regarded as "well-defined" (see [Sect. 1.2.2](#)). In such cases, the average values and their uncertainties have been re-estimated and listed.

In summary, notwithstanding all possible caution in estimating a "reasonable" uncertainty in each of the geometric parameters obtained by electron diffraction, they can never be immune from hidden systematic errors. Accordingly, a warning has to be given that a minority of the listed uncertainties may have been underestimated and that, in the worst cases, even some of the authors' conclusions may be qualitatively incorrect.

1.5 Geometric structures of molecules in excited electronic states

In surveying the information on excited states given in these tables the reader may be struck by its limited extent and apparently haphazard distribution when compared with the analogous compilation for stable molecules in their ground states. The reasons are well known but are none the less worth being briefly repeated, to be borne constantly in mind when trying to assess the meaning or reliability of the data in any particular case. There are two principal sources of difficulty, technical and theoretical.

Experimentally the source of information is almost exclusively spectroscopic. *Band-systems* may show *vibrational* and *rotational* structure whose analysis yields information on molecular geometry. Additional structure, such as electronic spin *fine-structure* or nuclear *hyperfine* structure, may be of great value in determining the molecular electronic structure but rarely contribute much to the knowledge of geometry. It may, however, greatly complicate the process of spectral analysis as a whole, making it difficult to extract the desired geometric parameters or limiting their accuracy: examples are to be found in NO₂ or triplet H₂CO.

Experimental limitations on the sources of primary information are usually chemical rather than instrumental. Thus chemically unstable species may be hard to prepare even in sufficient transient optical density or emitting concentration to yield a spectrum. More seriously, to obtain spectra of isotopic species usually requires the preparation of much larger samples than would be needed, *e.g.*, in microwave spectroscopy, and in dominating concentration rather than as a minor constituent of a mixture or even in natural abundance. Thus in molecules with numerous geometric parameters to be determined, the technique of isotopic substitution has, with the exception of deuteration, been used only relatively rarely (see *e.g.*, s-tetrazine). There are therefore in the literature many cases of molecules not listed here for which one or several rotational constants are known in excited states.

Instrumentally, limitations are rarely set by available resolving-powers. Spectra may be only partially resolved because of a combination of congestion and line-broadening: *e.g.*, through Doppler- and pressure-broadening; and, more seriously, due to unimolecular lifetime-limiting non-radiative processes such as pre-dissociation, pre-ionization or, in large molecules, electronic relaxation into dense vibronic manifolds of lower-lying electronic states, arising from the limitations of the Born-Oppenheimer approximation. It is this last factor which is responsible for the apparent paradox that more seems to be known about the excited electronic states of chemically unstable molecules, such as free radicals, than about those of the common stable molecules; for, as a simple rule, stable closed-shell molecules have only high-lying excited states, at energies comparable to or above those of bond dissociation energies, and hence spectra that tend to be diffuse through predissociation, whereas open-shell molecules such as free radicals have low-lying electronic states with sharp spectra in experimentally ideal regions. When spectra are rich and well-resolved, rotational constants may be obtained which, although still not as good as those from microwave spectra, are of considerable accuracy, for the relatively low precision of individual line-frequencies is to a degree compensated by the large number of lines usually observed (see *e.g.*, glyoxal). Where ground-state constants are known from microwave spectroscopy, excited-state constants may be obtainable with comparable accuracy, for it is usually possible to determine differences of rotational constants much more precisely than the constants themselves (see *e.g.*, propynal).

Theoretically, the interpretation of geometric parameters tends to be hedged by qualifications. Most directly, the constants of *rotational analysis* may be interpreted in terms of average moments of inertia as

in microwave spectroscopy except that the data tend to be much less extensive. From rotational constants A_v , B_v , C_v are calculated structures r_v which are effective averages over vibrational amplitudes in the level v . The level v is most often the zero-point level, and hence most of the structures quoted in these tables are the so-called " r_0 -structures" (see [Sect. 1.3.1](#)). As in ground states, r_0 -structures differ rather little from "true" r_e -structures in molecules that are relatively rigid; but in contrast, "non-rigid" molecules are much more common in excited states than in ground states. Many of the classical analyses involve quasilinear or quasiplanar structures, where r_0 -structures may differ considerably from r_e -structures. A striking example is to be found in the first excited quasiplanar singlet state of formaldehyde, in which the out-of-plane angles θ_0 and θ_1 are about 20° and 36° , respectively. Non-rigidity is often revealed by considerable inertial defects in planar molecules, but otherwise rotational analysis tends to be insensitive to the degree of non-rigidity and hence a poor way of determining "true" molecular structures in such cases.

Patchy but much more extensive information about potential surfaces as a whole may be obtainable from *vibrational analysis*. Electronic excitation usually leads to some changes of molecular geometry and these are reflected in the spectra by progressions of bands associated with transitions to a range of successive vibrational levels in a potential well to which their intensities are related through the *Franck-Condon Principle*. A knowledge of frequencies, assignments and intensities allows therefore in principle to map the potential surface of one electronic state onto that of another, *i.e.*, to determine structures relative to each other. In practice, there are great difficulties, and structures determined with any precision and completeness by these methods are very rare. There exists however an enormous literature giving partial indications of molecular structures of widely varying reliability, probability or interest. The simplest examples are cases in which a minimum statement can be made on the basis of observed selection-rules alone: that a molecule has "*changed shape*" on electronic excitation. By this is meant that the point-group symmetry of the nuclear framework at potential turning-points of *stable* equilibrium has changed, as in *e.g.*, linear-bent or planar-pyramidal transitions. Such behavior is now known to be rather common in polyatomic molecules and is usually regarded as interesting: the prototypes are in the first excitations of acetylene and formaldehyde. It also provides the cases in which the angular dependence of potential surfaces has been mapped out in greatest detail, with quite reliable estimates of equilibrium out-of-line or out-of-plane angles and barrier-heights between equivalent potential minima or conformers. Such structural information derived wholly from vibrational analysis has been included in these tables when regarded as of sufficient interest or reliability. The choice is necessarily arbitrary. Some idea of what structural information was available up to 1966 in other cases may be obtained from the tables in Herzberg's "Electronic Spectra of Polyatomic Molecules", General References [I-1], which lists molecules with up to 12 atoms according to their known electronic states rather than geometries; a review of the azines (aza-benzenes) by Innes *et al.* [57], and numerous articles devoted to the rotational analysis of complex electronic spectra by the technique of simulated computed band-contours mainly in "Journal of Molecular Spectroscopy" and "Molecular Physics". There is also a growing literature on the interpretation of the vibrational structure of photoelectron spectra which gives some information on the geometries of positive ions, but the results are only rarely definitive.

There has been great progress both in the experimental techniques of electronic molecular spectroscopy and in the theoretical techniques of analyzing spectra.

Experimentally, there have been several advances. The availability of narrow-line tunable lasers has transformed absorption spectroscopy. Instead of monitoring the dependence of the absorption-coefficient on spectral frequency in terms of Beer-Lambert attenuation of incident white light intensity in the conventional way, the absorption is detected through the fluorescence that it induces in the excited molecules. The sample is illuminated by a laser whose wavelength can be tuned continuously through the molecular absorption-spectrum and the total undispersed fluorescence is detected. The *laser-induced fluorescence spectrum* (LIFS) is thus simply related to the absorption spectrum except that the fluorescence intensities do not accurately reflect the absorption intensities since the fluorescence efficiencies of excited state levels depend on the extent to which these levels are mixed with high rovibronic levels of the ground state. The main advantages over conventional spectroscopy lie in sensitivity and resolution. Absorption of photons by molecules being a two-body process, the enormous radiation-intensity at the focus of a laser-beam will produce photon-absorption in a large proportion of the molecules present, even if few in number; and photoelectric detection of undispersed fluorescence can be taken down to single-

photon counting levels. LIF spectroscopy can therefore be as much as ten orders of magnitude more sensitive than ordinary absorption spectroscopy in terms of either molecular number-density or sample-volume. The linewidths of tunable lasers can be made very narrow, sharper than the widths of absorption lines broadened by Doppler effect and pressure broadening. Doppler-limited spectra are therefore replacing those which earlier were instrument-limited.

A further refinement uses countercurrent two-photon absorption which selects only molecules with negligible components of thermal velocity in the beam-direction, as in Lamb-dip spectroscopy. Such *sub-Doppler two-photon LIF spectra* have been obtained *e.g.*, for benzene (q.v.) in its near ultraviolet spectrum down to within a factor of only four times the natural homogeneous linewidth, in this case 2 MHz, with an effective resolution of 1.2×10^8 [58]. Spectral bands seen previously only as contours of partially resolved rotational structure now have the simplicity of those of fully-resolved spectra of diatomic molecules. Rotational constants are improved by nearly two orders of magnitude, enough to pick up quite precisely an inertial defect in what, at equilibrium, is indisputably a planar symmetric rotor. But the problem of determining "the molecular geometry of the molecule" is taken little further, being merely projected into the same field of uncertainties and ambiguities revolving around r_v - versus r_e -structures familiar in microwave spectroscopy.

The above techniques are restricted to molecules which fluoresce. A more general technique is *multiphoton ionization* (MPI) in which a molecule absorbs several photons sufficient in energy to produce a molecular ion. This technique is very sensitive since single ions can be detected. The process may involve a single laser and several photons, or two (or more) lasers with various combinations of photons, *e.g.*, 1+3, 2+2. One of the lasers can be adjusted so as to involve an intermediate excited state in which case the sensitivity is considerably enhanced and the process is known as *resonance enhanced multiphoton ionization* (REMPI). The detection of the resulting ion with a mass-spectrometer further refines the specificity of the method and allows individual mass peaks, and isotopic species, to be monitored. The introduction of ZEKE (*zero electron kinetic energy* [59]) considerably increases the resolution which is beginning to approach the limit imposed by the widths of the laser.

Another technique involves high-resolution rotational coherence spectroscopy (RCS), which records spectra as a function of time rather than frequency. The latter is then obtained by Fourier transformation. Spectra can be obtained by the method of time-resolved fluorescence depletion (TRFD) or by (1+1') pump-probe ionization (PPI) experiments. The technique has been applied to large molecules and complexes, such as the phenol dimer.

The application of these techniques is considerably enhanced by the introduction of sample-seeded supersonic jets. Gas-phase spectra are obtained at effective temperatures close to the absolute zero and the problem of "Boltzmann congestion" is effectively overcome. Besides making the analysis of previously hopelessly congested spectra tractable, it has revealed a new family of weakly-bound van der Waals dimers or clusters. Some of the analyses are limited to general conclusions, as *e.g.*, the distinction between end-on and sideways-on orientation of diatomic iodine in a benzene-iodine complex. Such data are not included in the present compilation. Other analyses, however, yield accurate internuclear distances as in the benzene-rare gas complexes.

Theoretically, the advances in computational methods have made possible more direct approaches to structural analysis. In the past, analysis was done by inversion. Spectral data were reduced to parameters such as rotational and vibrational constants. These in turn were inverted into other parameters that describe parts of molecular (Born-Oppenheimer) potential surfaces, such as the coordinates of their minima – the r_e -structures defining molecular geometry – and their curvatures around these minima – the "molecular force-field". These inversions involve many approximations, usually based on perturbation-theory, and tend to be ill-determined, leading to serious ambiguities. As examples, the separation of rotation and vibration was successful only in quasi-rigid molecules, as discussed at various places in the introduction above; and the treatment of molecular geometry in electronically degenerate or nearly-degenerate states confined to cases in which the vibronic interactions such as Jahn-Teller or Renner-Teller couplings were either very small or very large. Today the tendency is towards a more direct approach. A model potential surface is assumed, more and more frequently itself obtained from *ab initio* calculations (*e.g.*, in H_3 , q.v.), and rotational-vibrational energies calculated from it by direct diagonalization of large Hamiltonian matrices are compared with experimental values. The model is refined by itera-

tion. Semirigid molecules can be successfully treated (see *e.g.*, CH₂ and CH₂O), and Jahn-Teller effects have at last been convincingly analyzed in complex polydimensional systems such as C₆F₆⁺ [60].

As previously, precise meaning of the data quoted in the present tables is likely to vary from case to case as are the uncertainties where indicated. The reader wishing to use them beyond the level of ordinary general purposes is therefore advised to return to the original sources and to evaluate these for himself.

1.6 Arrangement of the tables

1.6.1 General remarks on the content

All information on one molecule is listed together. Gross formula, name and symmetry are given as headline. The molecule is identified not only by its names (see [Sect. 1.6.4](#)) but also by a schematic structural formula and/or a figure. After the symbol for the used experimental method follow tables with data. Further information and/or comments are added in remarks and footnotes, followed by the references to the original papers used as source of information. When results of two experimental methods are given, these are presented separately, designated each by the appropriate symbol (see [Sect. 1.9.2](#)).

Recent analysis of geometric structures (especially those of complicated molecules studied by electron diffraction) is assisted by the structural parameters estimated by *ab initio* and DFT calculations (see [Sect. 1.2.2](#)). A representative quantum mechanical basis set among those employed in the original analysis is listed in each case.

1.6.2 Presentation of the data and comments

a) *Atoms* of the same kind are distinguished by numbers given in parentheses, such as C(1), C(2), or sometimes designated by primes, *e.g.*, C(1), C(1'). Simple designations are used for hydrogen atoms; for example, H(s) and H(a) denote methyl hydrogen atoms located on a molecular symmetry plane and located out of plane, respectively. Non-equivalent hydrogen atoms in a methyl or methylene group are designated as H', H'',... and defined in a footnote or identified in the figure.

b) An *internuclear distance* is represented by a solid line, like C(1)–H(s) for a pair of directly bonded atoms, and by a dotted line as N(1)...N(2) for a nonbonded atom pair. A bond angle is represented as *e.g.*, C(1)–C(2)–O(1); other angles such as a dihedral angle are defined in each case.

Nonbonded internuclear distances are tabulated in almost all the electron diffraction papers considered, but only those nonbonded distances that have been determined precisely and that are regarded as especially important are listed in the tables together with bond distances and angles.

Distances are given in Å (1 Å = 0.1 nm = 100 pm); *angles* are given in degrees. The *uncertainty* in a structural parameter (see [Sect. 1.4](#)), given in parentheses, applies to the last significant figure(s) of the parameter; *e.g.*, 3.478(21) Å = (3.478±0.021) Å, 13.4(21) Å = (13.4±2.1) Å, 119.3(2) deg = (119.3±0.2) deg, and 119.3(20) deg = (119.3±2.0) deg.

c) *Atomic coordinates* (from microwave spectroscopy): For some molecules the atomic coordinates reported by the original authors are reproduced in the tables without change. However, the structural parameters are not necessarily consistent with the atomic coordinates, because authors may have chosen the final structures after allowing for the effect of vibration-rotation interaction. In many cases the coordinates are given – far beyond their experimental accuracy – to four to five decimals. No attempt has been made to evaluate errors in the coordinates. Hydrogen atoms are listed under the heavy atom to which they are bonded.

d) *Point-group symmetry* of each molecule is also given in the tables. For most fairly rigid molecules this is the symmetry of the nuclear framework at stable equilibrium, *i.e.*, of the minima of the interatomic potential surfaces. These minima define "the structure of the molecule" and act as the origins of the dis-

placement coordinates used to describe the (small) internal motions of the atoms in the vibrating molecule. There are $3N-6$ such coordinates for a nonlinear molecule containing N atoms and $3N-5$ for a linear molecule. The whole potential surface, in general, has several minima corresponding to what chemists distinguish as different isomers or conformers, depending on the topological relationship of local potential wells to each other. The symmetry of the whole potential surface is therefore always higher than that of its individual minima. If the potential barriers between minima are sufficiently low, the internal molecular motions may become delocalized over several potential minima, either by passing classically over the barrier as in *e.g.*, hindered internal rotations, or tunneling through them quantum-mechanically. To describe such motions it therefore often becomes convenient to use the symmetry-properties of an enlarged portion of the potential surface encompassing the several minima accessible to the motion. The point-group symmetry of a potential *maximum*, *e.g.*, between *equivalent* minima, is often a useful symmetry for this purpose, then referred to as the "effective symmetry of the molecule". A classical example is ammonia which, in its electronic ground state "belongs to C_{3v} " because the equilibrium configuration of its hydrogen atoms about the nitrogen atom is a trigonal pyramid. But there are clearly two equivalent pyramidal potential minima disposed symmetrically about a planar trigonal potential maximum, a potential turning-point at which the molecule has, instantaneously or at unstable equilibrium, the symmetry D_{3h} . If the molecules were rigid and the hydrogen atoms distinguishably labeled, the two pyramidal isomers would be optically resolvable *d* and *l*-isomers. As it is, the barrier is low, and the hydrogen atoms tunnel through it in a time which is short enough to make it necessary for some purposes to consider them as delocalized explicitly. For these – mainly spectroscopic – purposes the "effective symmetry of the molecule" is D_{3h} . For other purposes, such as a discussion of bulk dielectric properties reducible to an effective molecular electronic dipole moment, the effective symmetry remains C_{3v} . The point of these remarks is to stress again the well known fact that the selection of an appropriate symmetry depends on the barrier-height which a molecule has to overcome in going from one equilibrium form to another (the criterion of *feasibility*), and the purpose to which the symmetry properties are to be applied [61]. Conversely, in non-rigid molecules it may be quite difficult to establish the point-group symmetry at stable equilibrium – particularly when the potential barriers between minima do not even rise above the zero-point levels. A few cases of low barriers are annotated in footnotes.

Equilibrium symmetry is sometimes deduced by electron diffraction. Spectroscopy is often a better source of experimental information on symmetry. In other cases, where symmetry is simply *assumed*, explicit remarks are made on this effect; borderline cases are often encountered, however. For example electron diffraction data are often found to be "consistent" or "compatible" with a model of certain symmetry.

e) *Temperature* (with electron diffraction data): Since the geometric parameters determined by electron diffraction are thermal average values, they depend on the effective vibrational temperature of the sample molecules. Therefore, the temperatures of the experiment are listed explicitly whenever they are given in the original paper. The difference between the nozzle temperature and the effective temperature of the sample molecules depends on the experimental conditions such as the nozzle shape but is usually not essential. However, this temperature dependence is significant only when the experiment is done at very high temperature and/or when a property is examined which is very sensitive to temperature, such as the relative abundance of isomers in a conformational equilibrium.

f) *Mean amplitudes* (from electron diffraction data): All current papers of electron diffraction report the observed or calculated mean amplitudes; no data are given in the tables.

g) *Wavenumbers* of the vibrational modes related to intermolecular bonds in weakly-bound complexes provide valuable information on their structure and bonding properties. Therefore, the wavenumbers and the force constants for the bond-stretching mode, denoted as ν_s and k_s , respectively, are listed whenever accurate experimental values have been reported. In some cases the force constants for other intermolecular vibrational modes such as bending have also been determined.

h) *Methods and basis sets used in quantum chemical calculations* are listed, in most cases with abbreviations taken from original papers, if they were used in the analysis of experimental data.

1.6.3 Order of molecules

In subvolume II/28A, molecules containing no carbon atoms are arranged alphabetically according to their gross stoichiometric formulae. All molecules containing one or more carbon atoms, listed in subvolumes II/28B, C and D, are arranged according to the Hill system.

1.6.4 Nomenclature

The names of molecules are mostly taken from the original papers, but an attempt is made to follow the usage in Chemical Abstracts and the rules of IUPAC (International Union of Pure and Applied Chemistry). Therefore many molecules have two or three names listed.

A complex or an addition compound consisting of n , m ,... atoms or molecules is indicated by the notation ($n/m/\dots$), e.g., argon – hydrogen bromide (1/1).

1.6.5 Figures and structural formulae

Nearly all molecules are represented by a schematic structural formula with chemical symbols or a figure with circles representing atoms, where the symbols of hydrogen atoms are sometimes omitted. All figures have been prepared for this volume using a computer software. In cases where atomic coordinates are listed, the figure shows at least two of the coordinate axes, except where axes are self-evident or missing in the original paper. In both structural formulae and figures, the special designations (numbers, *etc.*) of individual atoms are assigned whenever necessary for discrimination. The numbers are very often based on those given in the original papers, and are consistent with those used in the respective tables. In many cases, however, they are modified to be consistent with the international recommendations.

The drawn lines connecting atoms in structural formulae do not necessarily need to represent correct bond orders or bond types, for outside the realm of organic chemistry a bond type in a molecule, particularly in the case of a free radical or a molecule in an electronically excited state, may be ambiguous, contentious, indefinable or even meaningless although perfectly characterizable experimentally in terms of an attractive potential function. Double and triple bonds, *etc.*, indicated on structural formulae and in data tables are not necessarily correct representations of their bond nature.

1.6.6 Source of bibliographic information

MOGADOC ("Molecular Gasphase Documentation") database was used as a source of bibliographic information. The full version of MOGADOC, regularly updated in intervals of one year, presently contains *ca.* 35000 bibliographic references for microwave spectroscopy, molecular radio astronomy and gas phase electron diffraction since 1930 until 2005 and covers about 9000 inorganic, organic and organometallic compounds including numerical datasets for bond lengths and angles for about 7000 compounds. Features of the database are described elsewhere [62, 63]. An online demo version of MOGADOC is available at <http://www.uni-ulm.de/strudo/mogadoc/>.

1.6.7 Features of CD version

All the information of this volume is also stored on the CD-ROM in the attachment. In the printed version you have only access to structural information by means of the gross formula in the Hill system, whereas the electronic version offers several possibilities to access.

In order to run the CD-ROM the necessary program Acrobat Reader® 4.0 must be installed on hard-disk. Some versions for MS-Windows®, Macintosh® or UNIX® can be installed by the usual setup procedures, others or new free versions are available from <http://www.ADOBE.com>. After installation of a suitable reader version, start by double clicking on the respective executable program file.

Browsing

For browsing the information on CD, open the file ii28d_start.pdf in the main root of the CD-ROM. On the left side you see bookmarks leading you to the table of contents and to the introduction. By clicking on the bookmarks you reach the respective chapter. You can either go from page to page or use the finder. In the first case you can read the first page, the previous, the next and the last page, respectively, by clicking one of the icons in the menu bar.



Searching author names



If you are interested in all structures which were studied by a specific author, you click the icon with the large binocular (left) and write the name of the author into a search mask, for example **Smith**. Then the first document of this author is shown and the retrieved search terms are highlighted. The icons pictured on the right can be activated in order to go to the previous or next entry with the retrieved string.



Searching compound names

The program enables the user to find also substances with a specific name segment. If the string **benzyl** is entered in the search mask, only compound names are retrieved, which contain the desired string as a separate word, such as benzyl cyanide. If the search term is truncated such as **benzyl***, chemical names like benzylidenmethylamine are found. Moreover left truncation is possible, for example ***fluoride**, which retrieves compound names with fluoride, difluoride, trifluoride, *etc.* If you are interested in all fluorine compounds you can truncate the search term on the left and right side simultaneously: ***fluor***. Among the hits you can find names such as aminodifluorophosphine, difluoroamine, fluoro-sulfate, germanium difluoride, hypofluorous acid, *etc.*

Searching gross formulae

Last but not least, entries can be retrieved by searching gross formula in the Hill system, where the element symbols and their index numbers are separated by no blanks at all, such as **CaCl2** for CaCl_2 or **ClFH2** for ClFH_2 . For more complex searches, please use the exclusive Online Help of the Acrobat Reader® 4.0.

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1.9 Lists of symbols and abbreviations

1.9.1 List of symbols

A, B, C	Rotational constants (see Sect. 1.2.1)
$\tilde{X}, \tilde{A}, \tilde{B}, \tilde{C}$	Labels for electronic states, ground state labeled \tilde{X}
$\tilde{a}, \tilde{b}, \tilde{c}, \dots$	Labels for excited electronic states of spin-multiplicity differing from that of the ground state \tilde{X}
r	Internuclear distance ($X-Y$ = bond distance, $X\dots Y$ = nonbonded distance)
r_e	Distance between equilibrium nuclear positions
r_{av}, r_z, r_a^0	Distance between average nuclear positions (ground vibrational state, $v_1 = v_2 \dots = 0$)
r_α	Distance between average nuclear positions (thermal equilibrium)
r_0	Distance between effective nuclear positions derived from rotational constants of zero-point vibrational level ($v_1 = v_2 \dots = 0$)
r_s	Distance between effective nuclear positions derived from isotopic differences in rotational constants
r_m	Distance between effective nuclear positions derived from the mass-dependence method of Watson, very close to r_e for molecules without hydrogen atoms
r_m^p	Distance obtained by a slightly modified method of Harmony <i>et al.</i>
r_{le}	Distance related to the effective structure derived from isotopic moments of inertia after isotope-independent correction ε
r_g	Thermal average value of internuclear distance
r_a	Constant argument in the molecular term, Eq. (8), see Table 1.3.3
f, k	Force constant for a weakly bound complex
θ	Bond angle; for indices, see r . For example, θ_e, θ_z and θ_α represent angles defined by a set of three nuclear positions, equilibrium, average (ground vibrational state) and average (thermal equilibrium), respectively, and θ_a by a set of three internuclear distances r_a . Some electron diffraction papers report distances as r_g and angles as θ_α or θ_z .
k_s	Stretching force constant of an intermolecular bond of a weakly bound complex
ν	Vibrational wavenumber for a weakly bound complex
ν_s	Wavenumber of a stretching intermolecular vibration of a weakly bound complex

1.9.2 List of abbreviations

CEI	Coulomb explosion imaging	TRFD	Time-resolved fluorescence depletion
CRD	Cavity ring-down spectroscopy	UED	Ultrafast electron diffraction
DFT	Density functional theory	UV	Ultraviolet spectroscopy
ED	Electron diffraction	ZEKE	Zero kinetic energy photoelectron spectroscopy
FTS	Fourier transform spectroscopy		
IR	Infrared spectroscopy	<i>ac</i>	<i>anticlinal</i>
LIF	Laser-induced fluorescence	<i>ap</i>	<i>antiperiplanar</i>
LMR	Laser magnetic resonance	<i>ax</i>	<i>axial</i>
MM	Molecular mechanics calculations	<i>b</i>	<i>bending vibrational mode</i>
MW	Microwave spectroscopy	<i>b</i>	<i>bridge</i>
NMR	Nuclear magnetic resonance	CM	center of mass (complex)
PES	Photoelectron spectroscopy	cm	center of mass (molecule)
PFI	Pulsed field ionization	eq	equatorial
Ra	Raman spectroscopy	<i>s</i>	<i>stretching vibrational mode</i>
RCS	Rotational coherence spectroscopy	<i>sc</i>	<i>synclinal</i>
REMPI	Resonance enhanced multiphoton ionization	<i>sp</i>	<i>synperiplanar</i>
TPI	Two photon ionization (spectroscopy)	<i>t</i>	<i>terminal</i>