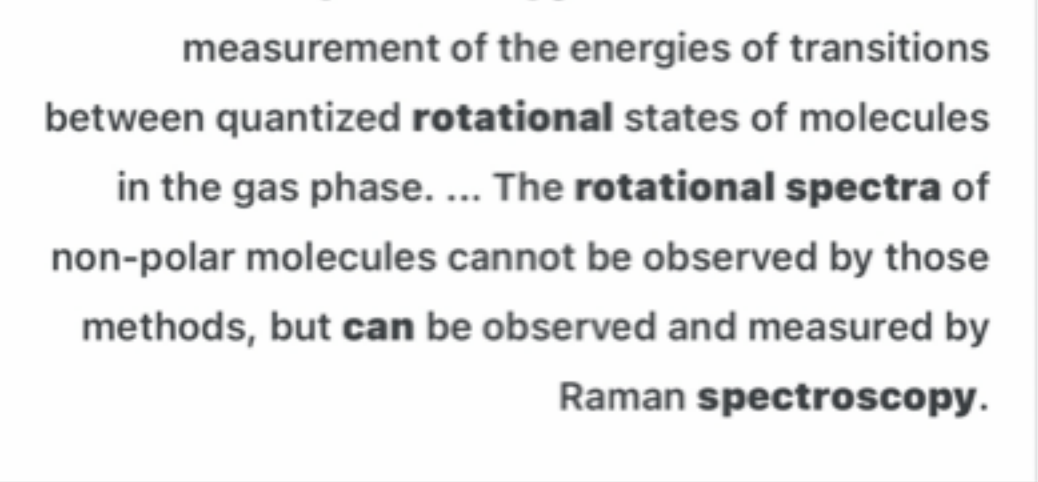
Rotational spectroscopy



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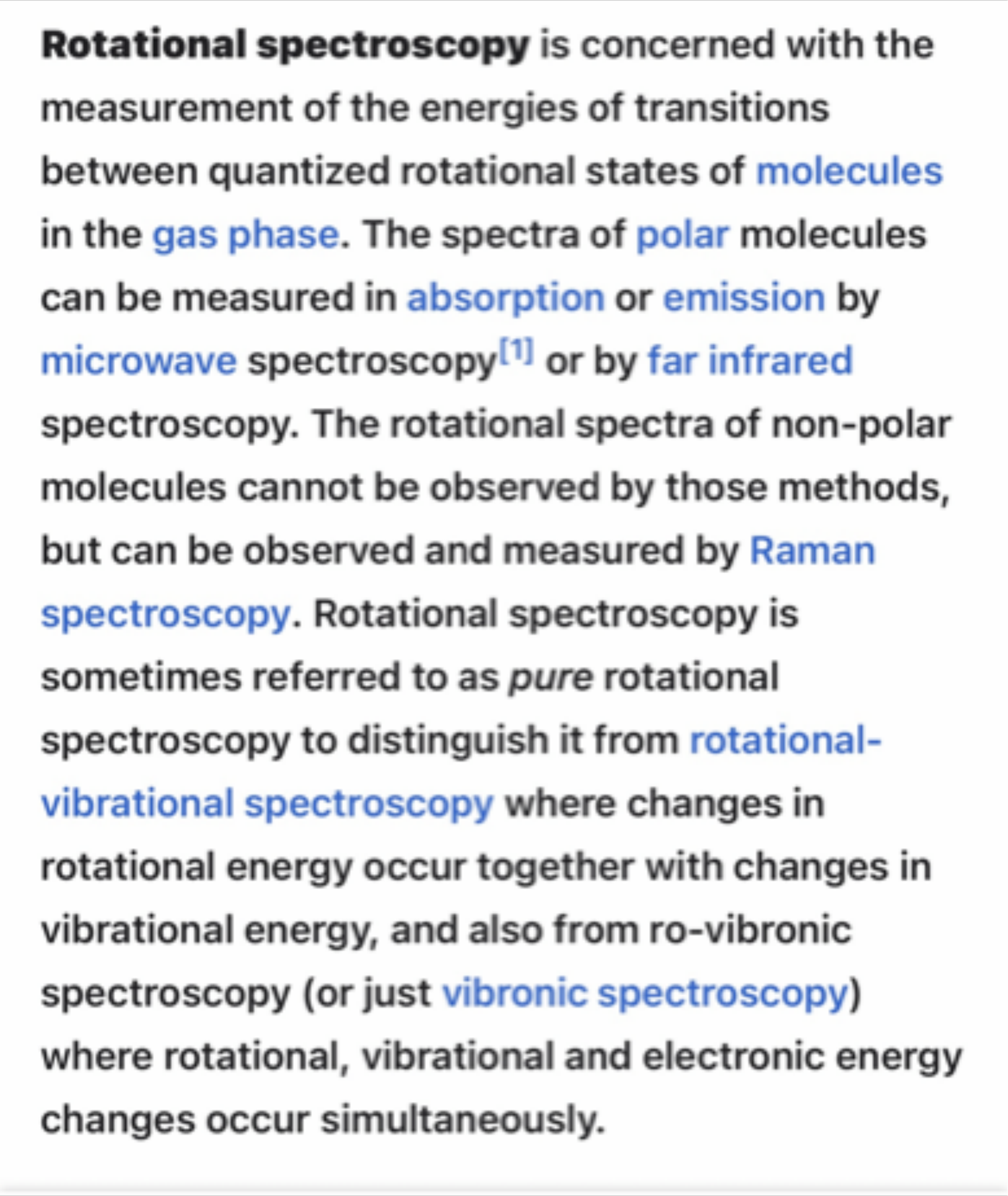
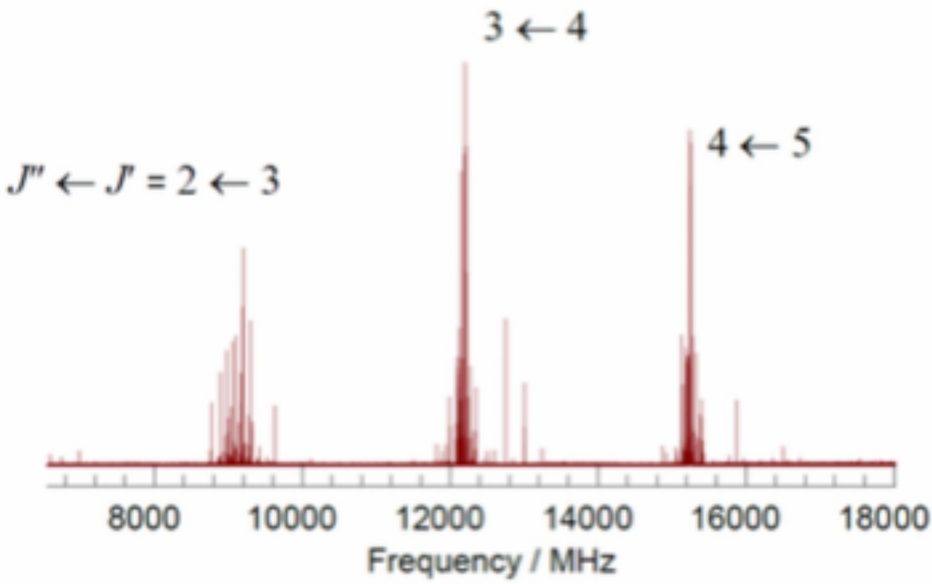
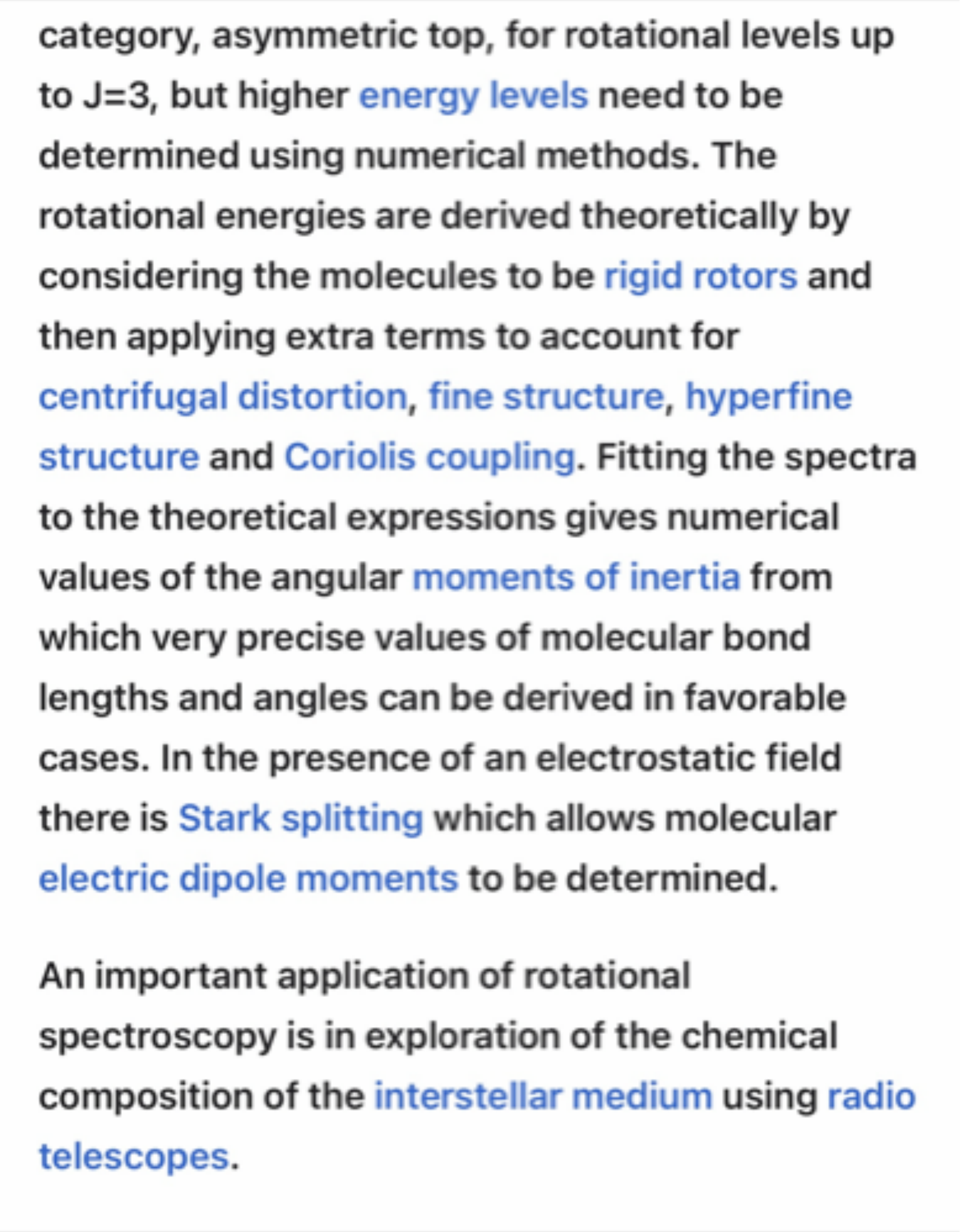


Rotational spectroscopy is concerned with the measurement of the energies of transitions between quantized rotational states of molecules in the gas phase. The spectra of polar molecules can be measured in absorption or emission by microwave spectroscopy[1] or by far infrared spectroscopy. The rotational spectra of non-polar molecules cannot be observed by those methods, but can be observed and measured by Raman spectroscopy. Rotational spectroscopy is sometimes referred to as *pure* rotational spectroscopy to distinguish it from rotational-vibrational spectroscopy where changes in rotational energy occur together with changes in vibrational energy, and also from ro-vibronic spectroscopy (or just vibronic spectroscopy) where rotational, vibrational and electronic energy changes occur simultaneously.



Part of the rotational spectrum of trifluoroiodomethane, CF_3I.[notes 1] Each rotational transition is labeled with the quantum numbers, *J*, of the final and initial states, and is extensively split by the effects of nuclear quadrupole coupling with the ^{127}I nucleus.

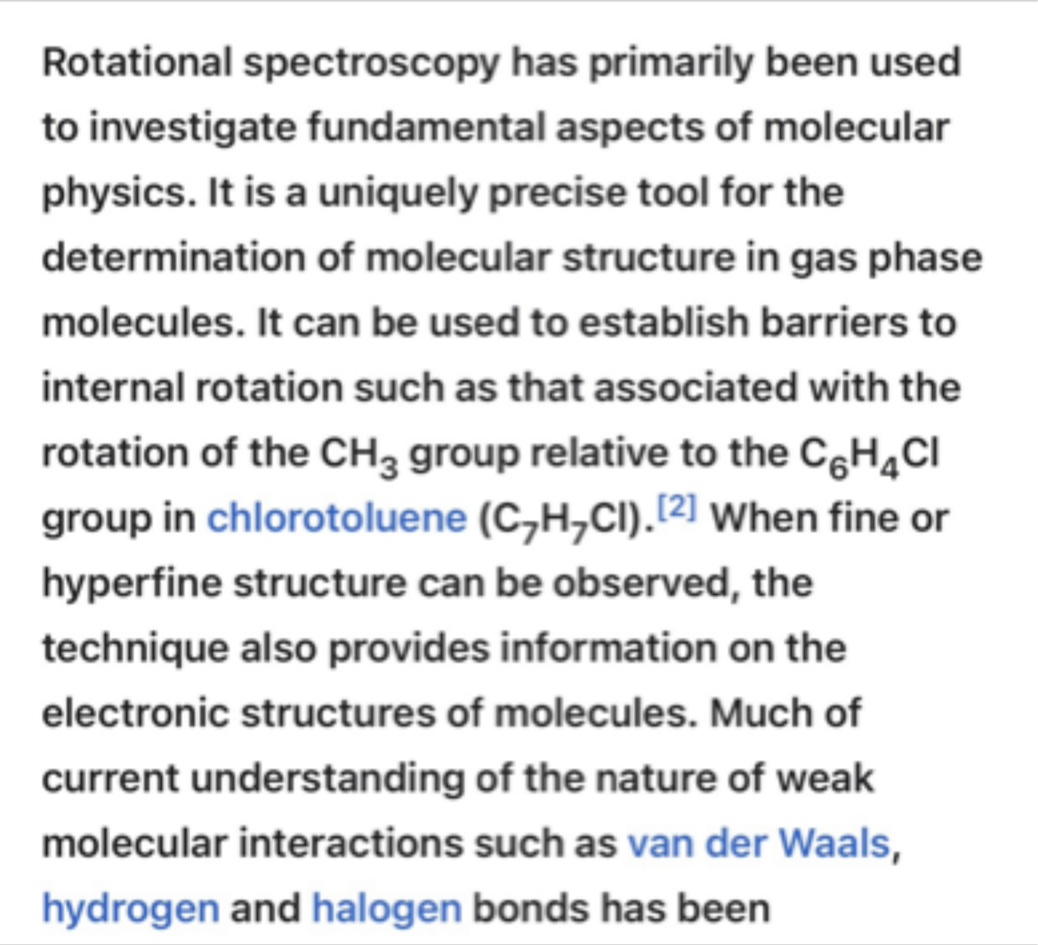
For rotational spectroscopy, molecules are classified according to symmetry into spherical top, linear and symmetric top; analytical expressions can be derived for the rotational energy terms of these molecules. Analytical expressions can be derived for the fourth



category, asymmetric top, for rotational levels up to J=3, but higher energy levels need to be determined using numerical methods. The rotational energies are derived theoretically by considering the molecules to be rigid rotors and then applying extra terms to account for centrifugal distortion, fine structure, hyperfine structure and Coriolis coupling. Fitting the spectra to the theoretical expressions gives numerical values of the angular moments of inertia from which very precise values of molecular bond lengths and angles can be derived in favorable cases. In the presence of an electrostatic field there is Stark splitting which allows molecular electric dipole moments to be determined.

An important application of rotational spectroscopy is in exploration of the chemical composition of the interstellar medium using radio telescopes.

Applications

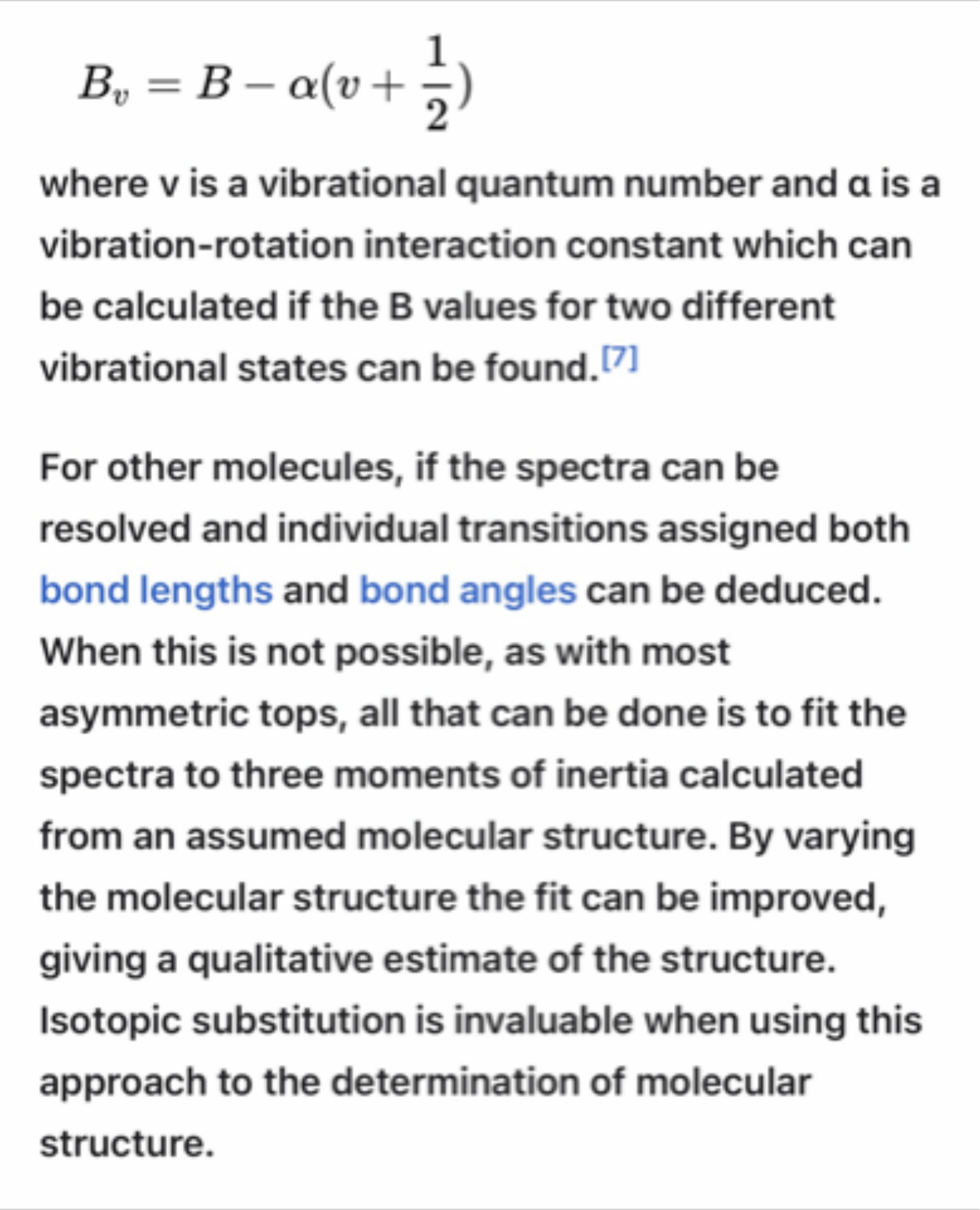


Rotational spectroscopy has primarily been used to investigate fundamental aspects of molecular physics. It is a uniquely precise tool for the determination of molecular structure in gas phase molecules. It can be used to establish barriers to internal rotation such as that associated with the rotation of the CH_3 group relative to the C_6H_4Cl group in chlorotoluene (C_7H_7Cl).[2] When fine or hyperfine structure can be observed, the technique also provides information on the electronic structures of molecules. Much of current understanding of the nature of weak molecular interactions such as van der Waals, hydrogen and halogen bonds has been established through rotational spectroscopy. In connection with radio astronomy, the technique has a key role in exploration of the chemical composition of the interstellar medium. Microwave transitions are measured in the laboratory and matched to emissions from the interstellar medium using a radio telescope. NH_3 was the first stable polyatomic molecule to be identified in the interstellar medium.[3] The measurement of chlorine monoxide[4] is important for atmospheric chemistry. Current projects in astrochemistry involve both laboratory microwave spectroscopy and observations made using modern radiotelescopes such as the Atacama Large Millimetre Array (ALMA).[5]

A molecule in the gas phase is free to rotate relative to a set of mutually orthogonal axes of fixed orientation in space, centered on the center of mass of the molecule. Free rotation is not possible for molecules in liquid or solid phases due to the presence of intermolecular forces. Rotation about each unique axis is associated with a set of quantized energy levels dependent on the moment of inertia about that axis and a quantum number. Thus, for linear molecules the energy levels are described by a single moment of inertia and a single quantum number, J, which defines the magnitude of the rotational angular momentum.

For nonlinear molecules which are symmetric rotors (or symmetric tops - see next section), there are two moments of inertia and the energy also depends on a second rotational quantum number, K, which defines the vector component of rotational angular momentum along the principal symmetry axis.[6] Analysis of spectroscopic data with the expressions detailed below results in quantitative determination of the value(s) of the moment(s) of inertia. From these precise values of the molecular structure and dimensions may be obtained.

For a linear molecule, analysis of the rotational spectrum provides values for the rotational constant[notes 2] and the moment of inertia of the molecule, and, knowing the atomic masses, can be used to determine the bond length directly. For diatomic molecules this process is straightforward. For linear molecules with more than two atoms it is necessary to measure the spectra of two or more isotopologues, such as $^{16}O^{12}C^{32}S$ and $^{16}O^{12}C^{34}S$. This allows a set of simultaneous equations to be set up and solved for the bond lengths).[notes 3] A bond length obtained in this way is slightly different from the equilibrium bond length. This is because there is zero-point energy in the vibrational ground state, to which the rotational states refer, whereas the equilibrium bond length is at the minimum in the potential energy curve. The relation between the rotational constants is given by



$$B_v = B - \alpha(v + \frac{1}{2})$$

where v is a vibrational quantum number and α is a vibration-rotation interaction constant which can be calculated if the B values for two different vibrational states can be found.[7]

For other molecules, if the spectra can be resolved and individual transitions assigned both bond lengths and bond angles can be deduced. When this is not possible, as with most asymmetric tops, all that can be done is to fit the spectra to three moments of inertia calculated from an assumed molecular structure. By varying the molecular structure the fit can be improved, giving a qualitative estimate of the structure. Isotopic substitution is invaluable when using this approach to the determination of molecular structure.

Classification of molecular rotors

In quantum mechanics the free rotation of a molecule is quantized, so that the rotational energy and the angular momentum can take only certain fixed values, which are related simply to the moment of inertia, I, of the molecule. For any molecule, there are three moments of inertia: I_A, I_B and I_C about three mutually orthogonal axes *A*, *B*, and *C* with the origin at the center of mass of the system. The general convention, used in this article, is to define the axes such that $I_A \leq I_B \leq I_C$, with axis A corresponding to the smallest moment of inertia. Some authors, however, define the A axis as the molecular rotation axis of highest order.

The particular pattern of energy levels (and, hence, of transitions in the rotational spectrum) for a molecule is determined by its symmetry. A convenient way to look at the molecules is to divide them into four different classes, based on the symmetry of their structure. These are

- Spherical tops (spherical rotors) All three moments of inertia are equal to each other: $I_A = I_B = I_C$. Examples of spherical tops include phosphorus tetramer (P_4), carbon tetrachloride (CCl_4) and other tetrahalides, methane (CH_4), silane, (SiH_4), sulfur hexafluoride (SF_6) and other hexahalides. The molecules all belong to the cubic point groups T_d or O_h.

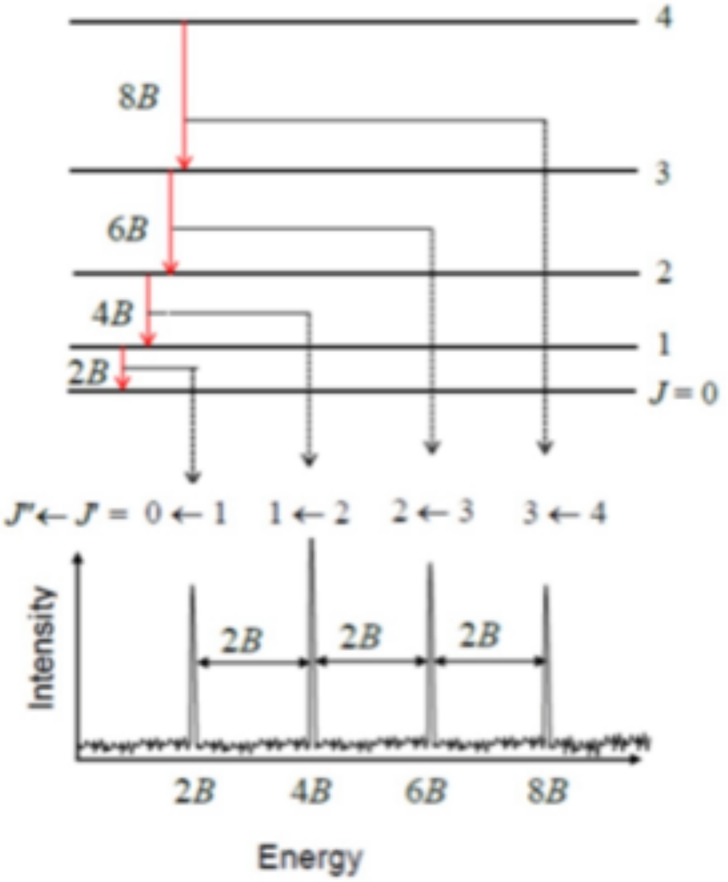
- Linear molecules. For a linear molecule the moments of inertia are related by $I_A << I_B = I_C$. For most purposes, I_A can be taken to be zero. Examples of linear molecules include dioxygen, O_2, dinitrogen, N_2, carbon monoxide, CO, hydroxy radical, OH, carbon dioxide, CO_2, hydrogen cyanide, HCN, carbonyl sulfide, OCS, acetylene (ethyne, HC≡CH) and dihaloethynes. These molecules belong to the point groups $C_{\infty v}$ or $D_{\infty h}$

- Symmetric tops (symmetric rotors) A symmetric top is a molecule in which two moments of inertia are the same, $I_A = I_B$ or $I_B = I_C$. By definition a symmetric top must have a 3-fold or higher order rotation axis. As a matter of convenience, spectroscopists divide molecules into two classes of symmetric tops, *Oblate symmetric tops* (saucer or disc shaped) with $I_A = I_B < I_C$ and *Prolate symmetric tops* (rugby football, or cigar shaped) with $I_A < I_B = I_C$. The spectra look rather different, and are instantly recognizable. Examples of symmetric tops include
  Oblate: benzene, C_6H_6, ammonia, NH_3, xenon tetrafluoride, XeF_4
  Prolate: chloromethane, CH_3Cl, propyne, $CH_3C{\equiv}CH$
  As a detailed example, ammonia has a moment of inertia $I_C = 4.4128 \times 10^{-47}$ kg m^2 about the 3-fold rotation axis, and moments $I_A = I_B = 2.8059 \times 10^{-47}$ kg m^2 about any axis perpendicular to the C_3 axis. Since the unique moment of inertia is larger than the other two, the molecule is an oblate symmetric top.[8]
- Asymmetric tops (asymmetric rotors) The three moments of inertia have different values. Examples of small molecules that are asymmetric tops include water, H_2O and nitrogen dioxide, NO_2 whose symmetry axis of highest order is a 2-fold rotation axis. Most large molecules are asymmetric tops.

Spherical top

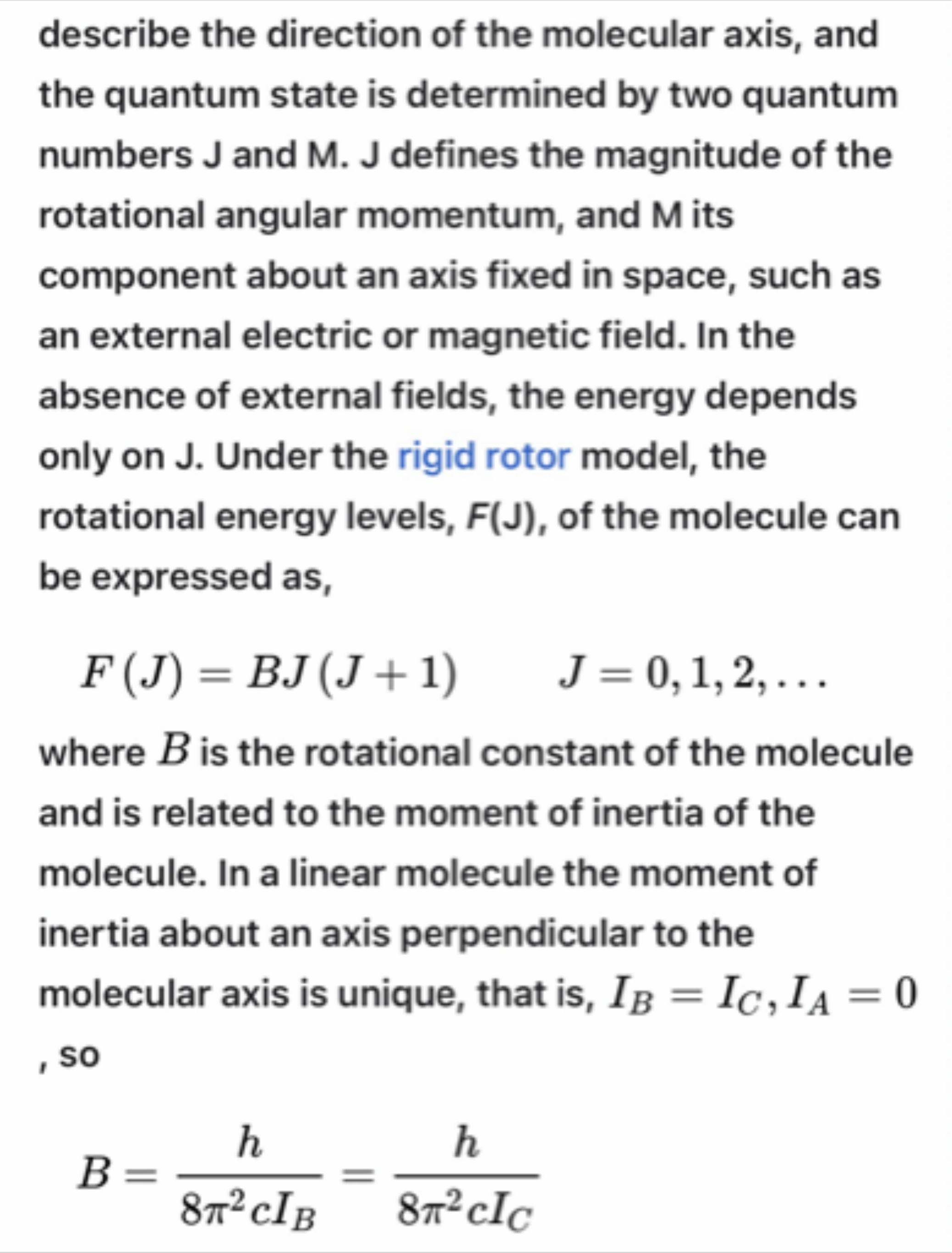
Spherical top molecules have no net dipole moment. A pure rotational spectrum cannot be observed by absorption or emission spectroscopy because there is no permanent dipole moment whose rotation can be accelerated by the electric field of an incident photon. Also the polarizability is isotropic, so that pure rotational transitions cannot be observed by Raman spectroscopy either. Nevertheless, rotational constants can be obtained by ro-vibrational spectroscopy. This occurs when a molecule is polar in the vibrationally excited state. For example, the molecule methane is a spherical top but the asymmetric C-H stretching band shows rotational fine structure in the infrared spectrum, illustrated in rovibrational coupling. This spectrum is also interesting because it shows clear evidence of Coriolis coupling in the asymmetric structure of the band.

Linear molecules



Energy levels and line positions calculated in the rigid rotor approximation

The rigid rotor is a good starting point from which to construct a model of a rotating molecule. It is assumed that component atoms are point masses connected by rigid bonds. A linear molecule lies on a single axis and each atom moves on the surface of a sphere around the centre of mass. The two degrees of rotational freedom correspond to the spherical coordinates θ and ϕ which

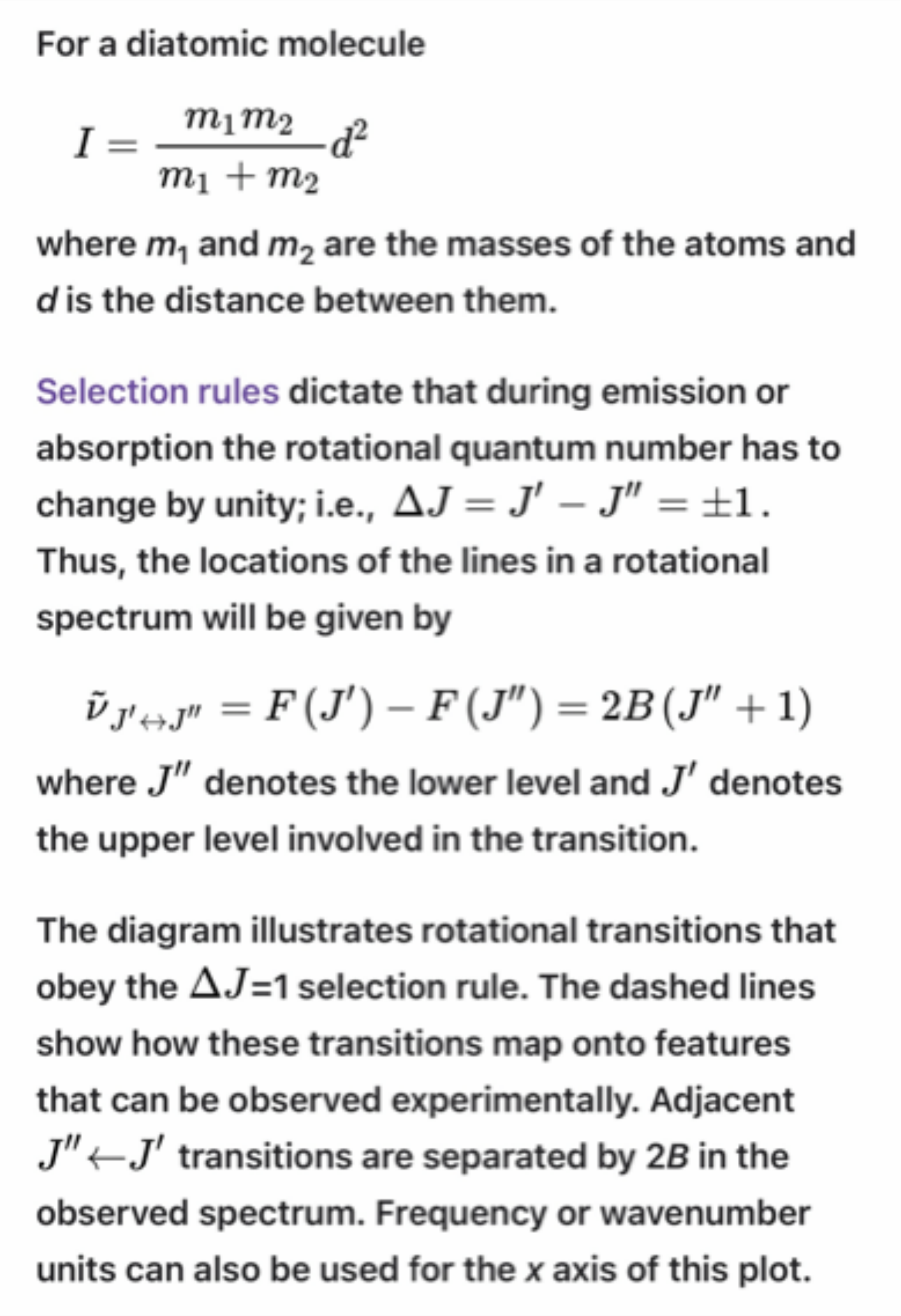


describe the direction of the molecular axis, and the quantum state is determined by two quantum numbers J and M. J defines the magnitude of the rotational angular momentum, and M its component about an axis fixed in space, such as an external electric or magnetic field. In the absence of external fields, the energy depends only on J. Under the rigid rotor model, the rotational energy levels, *F*(J), of the molecule can be expressed as,

$$F\left(J\right) = BJ\left(J+1\right) \qquad J = 0, 1, 2, \dots$$

where B is the rotational constant of the molecule and is related to the moment of inertia of the molecule. In a linear molecule the moment of inertia about an axis perpendicular to the molecular axis is unique, that is, $I_B = I_C, I_A = 0$, so

$$B = \frac{h}{8\pi^2 c I_B} = \frac{h}{8\pi^2 c I_C}$$



For a diatomic molecule

$$I = \frac{m_1 m_2}{m_1 + m_2} d^2$$

where m_1 and m_2 are the masses of the atoms and *d* is the distance between them.

Selection rules dictate that during emission or absorption the rotational quantum number has to change by unity; i.e., $\Delta J = J' - J'' = \pm 1$. Thus, the locations of the lines in a rotational spectrum will be given by

$$\tilde{\nu}_{J' \leftrightarrow J''} = F(J') - F(J'') = 2B(J'' + 1)$$

where J'' denotes the lower level and J' denotes the upper level involved in the transition.

The diagram illustrates rotational transitions that obey the ΔJ=1 selection rule. The dashed lines show how these transitions map onto features that can be observed experimentally. Adjacent $J'' \leftarrow J'$ transitions are separated by 2*B* in the observed spectrum. Frequency or wavenumber units can also be used for the *x* axis of this plot.