

The First Quantum Theory of Molecules

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Early quantum theories.

In 1912, Bjerrum published the first quantum theory of molecules, to treat the vibrational and rotational energies of diatomic molecules. That theory was incorrect but prepared the next stages of development of quantum mechanics.

The first quantum theory, which appeared in 1900, is considered to involve the derivation of a formula to represent the intensity of light emitted by a *black body* as a function of wavelength. Planck considered quanta of energy $h\nu$ emitted as radiation; h denoted the Planck constant. That formula, which describes a continuous distribution, is derivable without quantum assumptions [1]. Planck's theory employs harmonic oscillators as a convenient model, but their tangible relation to the physical experiment in which the radiation is emitted is at least questionable. The second quantum theory, which appeared in 1905, was Einstein's explanation of the photoelectric effect; he envisaged a beam of particles, each of energy $h\nu$ with Planck constant h and frequency ν , to be incident on a surface, from which, if the energy of one particle exceeded a particular threshold value characteristic of that surface, an individual electron is ejected with a kinetic energy proportional to the excess energy of that particle, subsequently called a photon. After one has recognized the quantum laws of nature, or the laws of discreteness [2], Einstein's treatment of that effect appears simple, but its value at its origin was that it was seminal in establishing such discrete or quantum properties.

The word *quantum* is derived from latin, meaning 'how much', but in English usage the term implies a *chunk*

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that is the smallest and indivisible unit of a physical quantity that retains the same properties. Apart from the radiation from a black body, the principal impetus to develop quantum theories resulted from the observations of discrete spectral lines, first by Wollaston in 1802. In 1885, Balmer deduced a formula to represent the inverse wavelengths of four lines in the emission spectrum of atomic H in terms of integer parameters; in 1886, Deslandres construed nearly linear separations, in terms of wavenumbers, of bands in the emission spectrum of molecular CN radicals, again with integer parameters.

Niels Bjerrum (1879–1958) was a Danish chemist who taught inorganic chemistry to Niels Bohr in the University of Copenhagen before a long association with the Royal Agricultural College first as professor and, subsequently, rector. Bjerrum had diverse interests in inorganic and physical chemistry and in molecular physics [3], and made many significant contributions to research throughout his career. In his early years, Bjerrum visited laboratories abroad, notably those of Ostwald in Leipzig, of Werner in Zurich and of Nernst in Berlin. In the latter institution in 1912, Bjerrum measured the thermal capacities of gases at elevated temperatures and sought a derivation of the variation of thermal capacity with temperature. Chemists were accustomed to think of molecules as static entities, but Clausius had proposed a dynamic model in which molecules vibrated and rotated, in accordance with the recognition by Newton that “light emitted by a heated object is performed by the vibrational motion of its parts”. Bjerrum was aware of the composite nature of bands in infrared absorption spectra of simple gaseous substances, such as HCl, whereby a sequence of lines comprises such a band. Bjerrum associated such a band with the vibration of a diatomic molecule and superimposed rotational motions. The rotational energy of a molecular dipole with

Bjerrum taught
Bohr.



Residual rotational
energy?

moment of inertia I was thus expressed [4] as

$$E = I(2\pi\nu)^2 = mh\nu$$

with frequency ν ; integer m imposes quantization. The rotational frequencies hence became

$$\nu_{\text{rot}} = mh/(4\pi^2 I).$$

Corresponding to two directions of rotation, emitted or absorbed frequencies would be given by a superposition of rotational frequencies on the vibrational frequency,

$$\nu = \nu_{\text{vib}} \pm \nu_{\text{rot}}$$

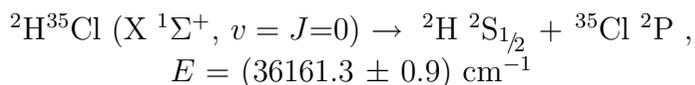
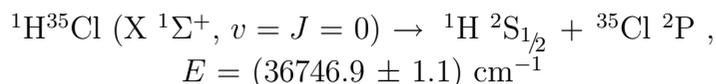
When infrared spectra of HCl were subsequently recorded with resolution sufficiently enhanced to exhibit a definite gap in the centre of the band, Bjerrum's theory seemed deficient, as there was no explanation of the lack of the purely vibrational frequency, ν_{vib} . Taken at its face value, Bjerrum's formula might imply an internuclear distance of 179 pm for HCl, following Rutherford's discovery of the nuclear atom in 1911, rather than a more accurate contemporary value of 127 pm. Although Bjerrum's formulation was then lauded for providing an explanation of the thermal capacities of gases, its reception was undermined when Kemble [5] recognised in 1920 that spectral frequencies are measures of energy differences, not identical to molecular frequencies. Kemble's criticism is equally applicable to Planck's model of a black body – the energies of the emitted photons are the differences of the energies of states of the emitters, but there is not necessarily any relation between the frequency of a photon and any frequency of the purported emitting 'oscillator'.

In any case, Bjerrum's first quantum theory of molecules, which concerned their vibration-rotational spectra and was published in 1912, preceded that of Bohr on the H atom in 1913, which was equally incorrect because of



compensating errors – an assumption of circular orbits of an electron and that the energy of the atom depended on a quantum number for the angular momentum of the electron about the atomic nucleus of H. Although Bohr's paper referred to the spectrum of the H atom and to Balmer's formula, which Bohr reproduced, that reference was an afterthought, because the rest of the paper had been composed before Bohr became aware of Balmer's result. Whereas Bohr's incorrect derivation is well known, Bjerrum's derivation is now practically forgotten. Despite efforts by Wilson and Sommerfeld to improve Bohr's treatment by including elliptical orbits, the progress toward a sustainable quantum theory of atoms and molecules resumed only in 1925 with Heisenberg's development of matrix mechanics, followed closely by Schrödinger's development of wave mechanics and Dirac's relativistic quantum mechanics.

Even now, not only chemists but also physicists typically maintain a blind spot that should have been eliminated with Kemble's wise observation [5], namely, a distinction between the frequencies (wavenumbers of lines in mid-infrared spectra multiplied by speed c of light) of those features and the 'vibrational frequencies' of molecules. With the simple case of a diatomic molecule, one can readily demonstrate a proof of this error; this proof has no relation to a harmonic oscillator or other theoretical artefacts, nor relies on any distinction between classical-mechanical and quantum-mechanical theories. The threshold energies to dissociate, for instance, HCl and DCl,



X and Σ are labels of states of the specified molecules.

Dissociation
energies of
HCl and DCl.



into their separate neutral atoms in their electronic ground states are moderately accurately measured, $(36746.9 \pm 1.1) \text{ cm}^{-1}$ for HCl and $(36161.3 \pm 0.9) \text{ cm}^{-1}$ for DCl, expressed in wavenumber unit (cm^{-1} is not a SI unit) [6]. The difference, $(585.6 \pm 2.0) \text{ cm}^{-1}$, between those minimum energies implies the existence of a residual vibrational energy in those molecular ground states, otherwise inaccessible to experimental measurement; this residual energy is best taken into account with this formula for vibrational energy $G(v)$ as a function of vibrational quantum number v that takes non-negative integer values;

$$G(v) = \sum_{j=0} C_j (v + \frac{1}{2})^j .$$

$G(v)$ is commonly presented in wavenumber unit, typically cm^{-1} , and coefficients C_j are fitted to reproduce optimally the differences of vibrational energy for as many states between which transitions are measured. The addend $1/2$ in $v + 1/2$ thus pertains to a residual vibrational energy, of magnitude

$$G(0) = \sum_{j=0} C_j (\frac{1}{2})^j ,$$

that a molecule possesses even in the discrete state of least vibrational energy, denoted with $v = 0$. Because the number of vibrational states for any diatomic molecule that dissociates into neutral atoms, rather than ions, is finite, and is in fact not large, this expansion is sufficiently convergent: the magnitudes of coefficients C_j decrease rapidly with increasing j . Under these conditions, the vibrational energy of HCl in its electronic ground state, relative to a hypothetical condition at which $G(v) = 0$, is equivalent to about 1443 cm^{-1} for $v = 0$, or 4329 cm^{-1} for $v=1$, and correspondingly increased values for further vibrational states. Molecule HCl has thus in no state a vibrational energy equivalent to 2886 cm^{-1} that marks the centre of the fundamental vibration-rotational band of gaseous HCl in the



mid-infrared spectral region. Likewise, the vibrational energy of DCl in a state with label $v=0$ is equivalent to 1045 cm^{-1} , and to 3135 cm^{-1} for the state $v=1$; there is no state with vibrational energy equivalent to 2090 cm^{-1} that marks the centre of the fundamental vibration-rotational band. The correlation of a feature of mid-infrared spectra of any other molecule with a vibrational frequency of the same value is equally fallacious, as is the typical output from a computer program for quantum chemistry that might purport to calculate such fundamental vibrational frequencies, generally with wavenumber as unit to compound the error.

Whether there exists a corresponding residual rotational energy is an unsettled question. In the early days of analysis of, for instance, infrared spectra of gaseous samples, there was a tendency to express the rotational energy within any vibrational state v as

$$F_v(J) = \sum_{j=1} B_j (J + \frac{1}{2})^{2j} ,$$

perhaps by analogy with the vibrational energy. A quantum-mechanical derivation of the energy of a rigid rotor was found to be proportional to $J(J+1) = (J + 1/2)^2 - 1/4$; despite the fact that no molecule is a rigid rotor, this purported theoretical basis led the spectroscopists at the time to prefer $J(J+1)$ to $(J + 1/2)^2$ as the variable in that expansion of rotational energy. Although subsequent detailed analyses of vibration-rotational spectra and their theoretical foundation [7] indicated a further contribution $1/4B_e$, i.e., a purely rotational contribution, to the residual energy when the rotational energies were expanded in terms of $J(J+1)$, the formulation of rotational energy in the latter form has persisted.

Suggested Reading

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