Wavefunction Collapse Broadens Molecular Spectrum

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Spectral lines in the optical spectra of atoms, molecules, and other quantum systems are characterized by a range of frequencies ω or a range of wavelengths *λ*=2*πc*/*ω*, where *c* is the speed of light. Such a frequency or wavelength range is called the width of the spectral lines (linewidth). It is influenced by many specific factors. Thermal motion of the molecules results in broadening of the lines as a result of the Doppler effect (thermal broadening) and by their collisions (pressure broadening). The electric fields of neighboring molecules lead to Stark broadening. The linewidth to be considered here is the so-called parametric broadening (PB) of spectral lines in the optical spectrum. PB can be considered the fundamental type of broadening of the electronic vibrational–rotational (rovibronic) transitions in a molecule, which is the direct manifestation of the basic concept of the collapse of a wavefunction that is postulated by the Copenhagen interpretation of quantum mechanics. Thus, that concept appears to be not only valid but is also useful for predicting physically observable phenomena.

Keywords: molecular spectrum ; electronic-vibrational level ; Franck–Condon principle ; collapse of wavefunction ; spectral line broadening ; adiabatic approximation ; polymethine dye ; linewidth

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In the theory of atomic spectra, the important concept of natural linewidth is introduced. Electrons can occupy discrete energy states in the atom. If an electron is in an excited state, it can jump to an energetically lower state by radiating a photon. The result of this is that the lifetime of the excited state is not infinite. In classical theory, the energy of an electron in such a system decays exponentially with time due to it experiencing radiative friction.

A dipole emitter (linear harmonic oscillator) with a frequency ω_0 is determined by the equation

$$\ddot{x} = -\omega_0^2 x - \gamma \dot{x} \tag{1}$$

with a radiative damping coefficient

$$\gamma = \frac{2\omega_0^2}{3c} r_e, \tag{2}$$

where $r_e = \frac{e^2}{4\pi\varepsilon_0 m_e c^2} \approx 2.818 \cdot 10^{-15}$ m is the electron's classical radius and m_e and *e* are the mass and modulus of the electron's charge, respectively. The solution of (1) is approximately ($\gamma \ll \omega_0$).

$$x = x_0 \exp\left(-\frac{\gamma t}{2} - i\omega_0 t\right). \tag{3}$$

The energy of the oscillator, averaged over one period, decreases exponentially (**Figure 1**a, smooth black curve)

$$W = \frac{1}{2} m(\dot{x}^2 + \omega_0^2 x^2) = W_0 \exp(-\gamma t). \tag{4}$$

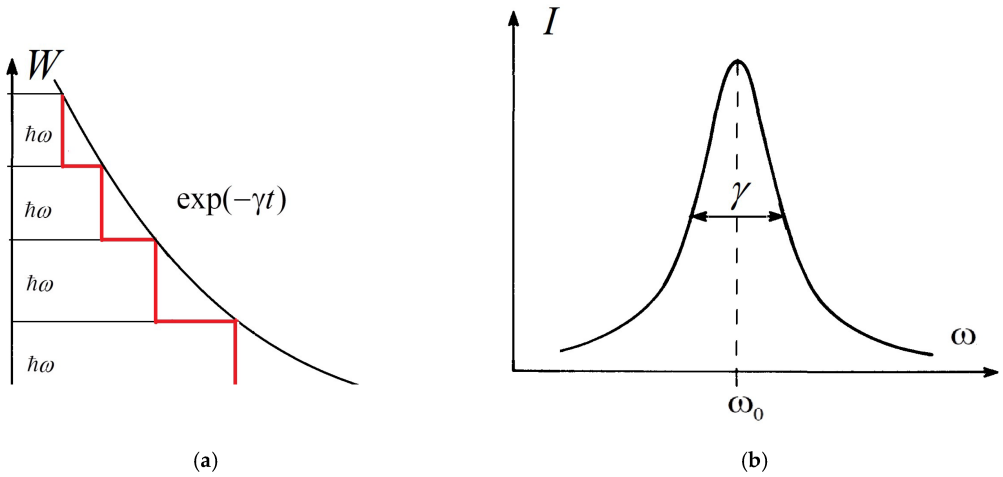

Figure 1. Natural linewidth in the theory of atomic spectra: (**a**) in the classical picture, all atoms of an ensemble radiate continuously and simultaneously (black smooth exponential curve); quantum emission of light occurs in portions (red step curve); (**b**) radiation intensity spectral distribution of a classical dipole emitter described by a Lorentzian line; the damping coefficient γ determines the characteristic width of the line.

The radiation intensity distribution of this dipole emitter is described by the so-called Lorentzian line (**Figure 1**b).

$$I = \frac{I_0}{(\omega - \omega_0)^2 + \gamma^2/4}. \quad (5)$$

The damping coefficient γ determines the characteristic width at half the height of the Lorentzian, i.e., the breadth at half the maximum intensity distribution. The linewidth introduced here is called the natural linewidth (Ref. [1], pp. 32–33). The atomic decay time (lifetime of excited state) is determined according to $\tau_0=\gamma-1$. The condition $\gamma \ll \omega 0$ expresses the fact that this time is very long compared with one period of the oscillator $2\pi/\omega 0$. For optical transitions, typical numerical values of τ_0 are 10^{-9}–10^{-8} s, and thus $\gamma=10^8$–10^9 s^{-1} (Ref. [2], p. 308).

Experiments carried out by Wilhelm Wien (1919) confirmed the approximately exponential attenuation of the luminescence of atoms, as well as the order of magnitude of the characteristic value of the coefficient *γ* [3]. However, the frequency dependence of the coefficient *γ* given by Formula (2) has not been experimentally confirmed (Ref. [4], p. 348; Ref. [5], p. 644).

According to quantum theory, an excited atom emits a photon instantly upon transition to a lower energy state. The duration of the emission or absorption process does not appear in the theory and is considered to be negligible. This may seem to be in direct contradiction to Wien's experiments. However, Wien's experiments determined the time of emission not of a single atom but of a large number of atoms simultaneously. For a large number of atoms or molecules, classical and quantum theories lead to qualitatively similar results. According to quantum concepts, each excited atom or molecule has a dark pause, during which the atom is in an excited state but does not radiate. Suddenly, the atom emits a photon instantly.

A quantum picture of the change in the energy of an ensemble of excited atoms with time is shown in **Figure 1**a (red step curve). That picture differs sharply from the classical one (black smooth exponential curve in **Figure 1**a). The duration of any dark pause corresponds to the lifetime of the excited state of the individual atom concerned. The lifetimes of atoms even in the same state are different and distributed according to statistical law.

Quantum emission of light occurs in quants. First, one atom emits a photon, then another, and so on. Thus, the curve looks like a staircase. The height of all the steps is the same, but the width of the steps fluctuates chaotically. Each step corresponds to the radiation of an individual atom. However, in the presence of a large ensemble of excited atoms, in practice, it is possible to use an exponential instead of a step curve, as in the classical theory. Thus, if there is a large number of atoms, N_0, in the same excited state, then the change in the number of atoms in the excited state is given approximately by an exponential law with decrement γ:

$$N = N_0 \exp(-\gamma t). \quad (6)$$

The natural linewidth in quantum theory is explained by the uncertainty of the corresponding energy of excited levels of the atom. Heisenberg's uncertainty relation can be written as $\Delta E\tau_0 \geq \hbar$, where $\tau_0 = \gamma^{-1}$. The ground state of the atom has an exact energy value, while the excited state has an energy uncertainty $\Delta E \geq \hbar\gamma$. The typical magnitude of γ in conventional spectroscopic units is 10^{-4} cm^{-1} (Ref. [2], p. 308), while the optical frequency is of the order of 10^4 cm^{-1}. The general expression for γ (Ref. [1], p. 184) is defined as follows:

where ρ_W is the density of energy of the excited atomic states, $|H^2|$ is the square of the matrix element of the interaction energy between electron and the electromagnetic field, and $\int d\Omega$ denotes integration over all directions of photon propagation.

Usually, two kinds of spectral-line broadening are considered [6]. Homogenous broadening is due to internal processes that broaden the optical lines in the spectrum of a single atom or molecule (e.g., radiative broadening that provides natural linewidth). Inhomogeneous broadening arises from the effects of the surroundings and external processes. For example, the stochastic electric fields of neighboring molecules lead to Stark broadening that manifests itself in fluctuations of the solvatochromic spectral shift [7][8], while Doppler broadening is due to thermal motion. It is generally accepted that all such broadenings are sufficiently small: many orders of magnitude smaller than the observed width of the optical absorption band of the molecule (10–10^3 cm^{-1}).

There are complex internal processes in molecules that are not present in single atoms. Therefore, molecular spectra, which have the form of bands, do differ significantly from atomic ones. This difference is due to the fact that electronic transitions are influenced by the vibrational-rotational motions of groups of atoms within the molecule. Rovibronic transitions merge into absorption and emission bands corresponding to the energy spectrum of a molecule of this type [6].

An accurate description of quantum transitions in molecules can only be made on the basis of taking into account all the requirements of modern quantum mechanics. Let us recall the basic principles of the Copenhagen interpretation of quantum mechanics (CI), which is taken as a basis by most modern scientists [9][10][11][12]:

1. The wavefunction includes complete information about quantum objects and their states (completeness principle).

2. A quantum state represented by the linear superposition of the quantum states can be considered as an admissible quantum state (superposition principle).

3. Quantum objects have certain pairs of complementary properties that cannot all be observed or measured simultaneously (Bohr's principle of complementarity).

4. Heisenberg's uncertainty principle.

5. Max Born's probability interpretation of squared wavefunction.

6. The quantum object under investigation is inseparable from the experimental device used to make the measurements. The interaction between the object and device forms an inseparable part of the quantum phenomena. The instantaneous collapse of the wavefunction (reduction of the wave packet) upon measurement is a manifestation of that inseparability principle.

7. Quantum and classical physics correspond to each other in the classical limit (Bohr's correspondence principle).

Electronic-vibrational (vibronic) transitions in molecules are usually described on the basis of the Franck Condon (FC) principle. Historically, this principle was introduced in the early years of quantum mechanics (1925–1928) [13][14][15][16] before CI was finally formulated.

Therefore, the theory of molecular spectra based on the FC principle does not consistently take into account the postulates of the CI, and, in particular, the FC principle ignores the very important concept of wavefunction collapse. According to Don Howard [16], that is not surprising because the concept of wavefunction collapse was finally formulated only in the mid-1950s by W. Heisenberg: 'Various other physicists and philosophers, including Bohm, Feyerabend, Hanson, and Popper, having further promoted the invention in the service of their own philosophical agendas.'

At the same time, the efficiency of the FC principle in the form in which it came into use in 1928 is proved by its satisfactory agreement with experiments on molecular spectroscopy [17][18][19][20]. However, a more consistent application of the postulates of the CI makes it possible to achieve a more detailed description in this area. In fact, the collapse of the wavefunction is manifested in so-called parametric broadening (PB) [21][22] that plays an important role in the formation of

molecular vibronic spectra. Herein, consider the mechanism of PB using the example of a (0–0) vibronic transition in a series of polymethine dyes.

Although the electronic-vibrational (vibronic) terms of a molecule shall be considered, the same conclusions can be drawn in the general case of electronic-vibrational-rotational (rovibronic) transitions. Furthermore, although only the absorption spectra shall be considered, the broadening of emission spectra can be determined in a similar way.

The problem of calculating the vibronic transition in the adiabatic approximation was considered in general form in [21][22]. It is also shown there how the collapse of the wavefunction at the moment of absorption or emission of a phonon leads to parametric broadening of the vibronic line. Herein, consider this problem in the simplest one-dimensional case.

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