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Using Spectroscopy to Understand Quantum Mechanics in Upper Secondary School: a Historical and Experimental Approach

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Abstract

The chemistry syllabus of the Italian Liceo requires teaching some quantum physics concepts in the third year, while quantum mechanics is taught in physics during the fifth year. Therefore, chemistry teachers should introduce quantum physics without using too many mathematical formalisms. This contribution aims to illustrate the usefulness of an approach centered on: at first on the milestones about spectroscopy, highlighting its usefulness for the knowledge of the atomic structure; secondly, on more recent spectroscopic experiments involving molecules. While the first part was carried out through lectures, during the second part the students worked in groups most of the time. The students appreciated this approach, as demonstrated by their interest, their numerous requests for clarification and by their answers to the teacher's questions.

Keywords: *quantum mechanics; spectroscopy; chemical education; physics education.*

1. Introduction

Introducing undergraduate science students to quantum physics without using mathematics tools they are not prepared for, is a necessity [1]. Even more challenging is dealing with the fundamental concepts of quantum mechanics in the classical and scientific Liceo, an Italian upper secondary school where historical-philosophical subjects are studied in depth: the chemistry syllabus of Liceo requires teaching these concepts in the third year, while they are taught in physics only in the fifth year. However, a first approach to quantum mechanics for chemistry teaching can be an advantage with the appropriate strategies [2]; for example, using a historical and experimental approach for spectroscopy.

The first part of the project here presented was realized through lectures on the historical importance of spectroscopy to show the existence of quantized energy at the subatomic level. The second part deals with the spectroscopic analysis of molecules starting from the practical laboratory sessions titled "Light and molecules", initially implemented within the PLS (“Piano Lauree Scientifiche”, Scientific Degrees Project) and training for career guidance actions called PCTO (“Percorsi per le Competenze Trasversali e l'Orientamento”, Routes for Transversal Competences and Orientation) [3] through a collaboration between Tor Vergata University and the Liceo Lucio Anneo Seneca (Roma) [4] during the academic year 2020/2021.

The entire sequence was later applied and improved in other schools (Liceo “E. Majorana” and Liceo “G. Marconi” of Latina) over the subsequent four academic years. All the activities were carried out by cooperative learning and peer-to-peer education methods.

The scientific sections were involved; anyway, the sequence takes into account very simplified models also suitable for the classical Liceo, where the time dedicated to scientific subjects is very limited. This sequence can be implemented after students have been introduced to the nature of electromagnetic radiation, the meaning of energy quantization, the atomic and molecular orbitals.

2. The Spectroscopy

Matter and light are intimately connected. Investigations into the structure of atoms began with the observation of their luminous effects observed through the spectroscope, invented by J. von Fraunhofer (1787-1826) in 1814. Studying the solar spectrum, Fraunhofer had recognized some particularly bright lines, attributed to hydrogen, present in abundance in the Sun [5]. Table 1 shows the wavelengths of four lines with the names given by Fraunhofer.

H_α	H_β	H_γ	H_δ
6563 Å	4861 Å	4340 Å	4102 Å

Table 1. Lines discovered by Fraunhofer in the solar spectrum

Subsequently, the study of light effects was extended to spectra obtained directly by thermal/electrical means, for example by means of a flame/voltaic arc, or by means of discharge tubes in rarefied gases. Discharge tubes were realized by W. Crookes (1832-1919), allowing an increasingly detailed study of the atomic structure, also made possible by the identification of X-rays and by the discovery of radioactive decay [6]. There are essentially three types of spectra [7]:

- the continuous spectrum, which includes all visible wavelengths, is produced mainly by the heating generated by the flame and the electric arc. It can also be observed by separating visible light into its components using Newton's prism.
- the line emission spectrum, formed of thin, well-defined lines, is typical of the emission of monoatomic gases in discharge tubes. Each chemical element has a characteristic line spectrum, a sort of identification “bar code”.
- the band spectrum, consisting of broad bands of light; it can be produced by the excitation of gaseous molecules in discharge tubes; even the molecules have a sort of “fingerprint”.

2.1 The Spectral Series

After Fraunhofer, several scientists contributed to broadening the knowledge of the hydrogen spectrum by gradually discovering the various spectral series, the set of spectral lines typical of some regions of the electromagnetic spectrum [5]: J. J. Balmer (1825-1898) in 1885 (visible region) followed by T. Lyman (1874-1954) in 1904 (UV), L. C. H. F. Paschen (1865-1947) in 1909 (IR), F. P. Brackett (1865-1953) in 1922 (extreme IR). Figure 1 reports some series with the name of their discoverers.

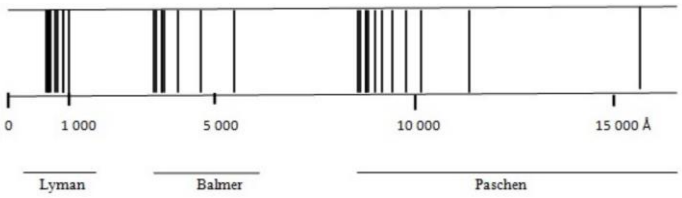

Fig. 1. The spectral series of hydrogen

Figure 1 shows line spectra, in which the energy associated with each radiation varies in a discrete way. Balmer proposed an empirical formula that allowed the lines to be classified into groups, the so-called Balmer formula:

$$1/\lambda = R\,(1/n'^2 - 1/n^2)$$

where λ is the wavelength, R is the Rydberg constant ($1{,}09737 \cdot 10^7$ m^{-1}), n' and n are positive integers other than zero (with $n > n'$). The nature of the values of n and n' further confirmed a “packaged” energy variation. Table 2 lists the series with the respective cut-off frequency values.

Series name	Spectral region	n’	N	Frequency limit
Lyman	ultraviolet	1	2, 3, 4, …	R
Balmer	visible	2	3, 4, 5, …	R/4
Paschen	infrared	3	4, 5, 6, …	R/9
Brackett	extreme IR	4	5, 6, 7, …	R/16
Pfund	extreme IR	5	6, 7, 8, …	R/25

Table 2. Hydrogen spectral series with limit frequency values as a function of the Rydberg constant

It was discovered that each hydrogen line could be obtained as the difference between terms in the Balmer formula, resulting in the so-called spectroscopic term Tn. This meant that the multiplicity of hydrogen lines could be deduced through all possible differences between a few fundamental frequencies; this observation was important in formulating the new atomic model of N. H. D. Bohr (1885-1962), since the model of E. Rutherford (1871-1937) presented several important critical issues due substantially to the use of continuous energy values. For hydrogen, the generic spectroscopic term was $Tn = R/n^2$ (Balmer's terms). The other atoms were less simple due to the multiplicity of the lines that often overlapped each other. However, Rydberg terms were derived for more complex atoms, in particular for the elements of group IA of Periodic Table (alkali metals): $Tn\alpha = R/(n + \alpha)^2$,

where α is an invariable correction constant for a whole succession of spectroscopic terms. It was decided to indicate the Rydberg spectroscopic terms in an abbreviated form, simply writing the numerical value of n and the symbol that distinguishes α for each series, for example:
$T_{2s} = R/(2 + s)^2 = 2s$ per $n = 2$, $\alpha = s$
$T_{3p} = R/(3 + p)^2 = 3p$ per $n = 3$, $\alpha = p$
$T_{4d} = R/(4 + d)^2$ per $n = 4$, $\alpha = d$
Bearing in mind that the sequence s could assume values starting from n = 1, p from n = 2, d from n = 3, f from n = 4 etc., the sequence of spectroscopic terms for a given atom is reported in Table 3.

1s	2s	3s	4s	5s	…
	2p	3p	4p	5p	…
		3d	4d	5d	…
			4f	5f	…
					…

Table 3. Sequence of spectroscopic terms of a given atom.

The sequence briefly outlined here is useful to illustrate in a simple way how the quantization of energy at the atomic level was deduced starting from macroscopic observations originating from the interaction between light and matter; the conclusions drawn were very important for the formulation of the Bohr model. Furthermore, the alphanumeric symbols used in Table 3 allow us to understand the orbitals denomination, matching energy levels expressed by the principal quantum number to the relative letter of the alphabet; this denomination is still used, within the subsequent quantum mechanical model of E. Schrödinger (1887-1961). The Schrödinger model explains not only the quantum nature of energy exchange, but also the wave properties of matter and the probabilistic nature of quantum mechanics laws (here omitted). For further information suitable for secondary school, it is possible to refer to other sources [5].

3. From Atoms to Molecules

Moving from atoms to molecules, optical spectroscopy seems the most suitable instrument to pursue an experimental approach to understand foundations of quantum mechanics of molecular properties [3]. As specified before, spectral bands are characteristic of molecules. The reported examples concerned the interaction between the electromagnetic radiation (electrical field component) and some simple molecular systems:

- carbon monoxide (CO) and chloroform/deuterated chloroform ($CHCl_3$/$CDCl_3$) for IR spectroscopy;
- thiacyanines for visible spectroscopy;
- acetone (C_3H_6O) for UV spectroscopy.

3.1 IR Spectroscopy

The infrared region of the spectrum extends from the long-wavelength end of the visible region at 1 μm out to the microwave region at about 1,000 μm. It is common practice to specify infrared vibrational frequencies in wavenumber units: $\tilde{\nu} = 1/\lambda = \nu/c$, where c is the speed of light, λ the wavelength and ν the frequency. Thus, this region extends from 10,000 cm^{-1} down to 10 cm^{-1}. The vibrational frequencies of most molecules lie in the range 4000 to 400 cm^{-1}.
The radiation from a source emitting infrared frequencies is passed through a sample of the material to be studied. When the frequency of this radiation is the same as a vibrational frequency of the molecule, the molecule may be vibrationally excited; this results in loss of energy from the radiation and gives rise to an absorption band. The spectrum of a polyatomic molecule generally consists of several such bands arising from different vibrational motions of the molecule. A diatomic molecule has only one vibrational mode. The simplest model of a vibrating diatomic molecule is a harmonic oscillator, for which the potential energy depends quadratically on the change in internuclear distance.
The allowed energy levels of a harmonic oscillator, as calculated from quantum mechanics are

$$E_{(v)} = h\nu\,(v + 1/2) \qquad (1)$$

where v is the vibrational quantum number having integer values 0, 1, 2, . . .; ν is the vibrational frequency, and h is the Planck constant.
The simplest model of a rotating diatomic molecule is a rigid rotor or “dumbbell” model in which the two atoms of mass m1 and m2 are considered to be joined by a rigid, weightless rod. The allowed energy levels for a rigid rotor may be shown by quantum mechanics to be

$$E_{(J)} = BJ\,(J+1) \text{ where } B = h^2/8\pi^2 I \qquad (2)$$

B is called the rotational constant; it is characteristic of the molecule under examination. The rotational quantum number J may take integer values 0, 1, 2, ... The quantity I is the moment of inertia, related to the internuclear distance r and the reduced mass $\mu = m_1\, m_2 / (m_1 + m_2)$:

$$I = \mu\, r^2 \qquad (3)$$

The vibrational frequency ω in wavenumbers is related to the speed of light c and the square root of the ratio of the oscillator force constant k to the reduced molecular mass μ:

$$\tilde{\nu} = 1/2\pi c\ (k/\mu)^{½} \qquad (4)$$

The harmonic-oscillator, rigid-rotor selection rules are $\Delta v = \pm 1$ and $\Delta J = \pm 1$; that is, infrared emission or absorption can occur only when these “allowed” transitions take place.

When a molecule is exposed to infrared radiation, specific frequencies are absorbed, causing the bonds within the molecule to vibrate. These vibrations, such as stretching, bending, and twisting, occur at characteristic frequencies for different functional groups (e.g., C=O, O-H, C-H). By analyzing the absorbed frequencies, IR spectroscopy provides valuable information about the presence and structure of these functional groups, aiding in the identification and characterization of unknown compounds.

3.1.1 The IR Spectrum of CO

Each molecule can perform a series of movements depending on the number of atoms N, that have 3N coordinates; in particular, CO molecule, being characterized by the presence of two atoms each having 3 coordinates, can perform 6 movements: 3 types of translations, 2 types of rotations and 1 type of vibration (stretching or bending). Each molecular movement is associated with a quantized vibro-rotational energy. The IR spectrum of carbon monoxide (CO) provides compelling evidence for the quantization [8].

At room temperature carbon monoxide populates many rotational levels; the most populated rotational level corresponds to J=9. Quantum mechanics ensures that, by interaction with electromagnetic radiation, the CO molecule can absorb energy only between adjacent levels: from a generic level J it is possible to absorb a photon to go up to the J+1 level, or to give up a photon and go down to the J-1 level. The vibro-rotational spectrum of the CO molecule is reported in Figure 2. The spectrum represents all the possible transitions between the rotational states of the fundamental vibrational level (v = 0) and those of the excited vibrational state (v = 1). The high energy band (left) represents all the rotational transitions of the J → J + 1 (R branch) type; the lower energy band (right) represents all the rotational transitions J → J - 1 (P branch) type. The absorption intensity shows a characteristic trend, caused by the different populations of the rotational levels.

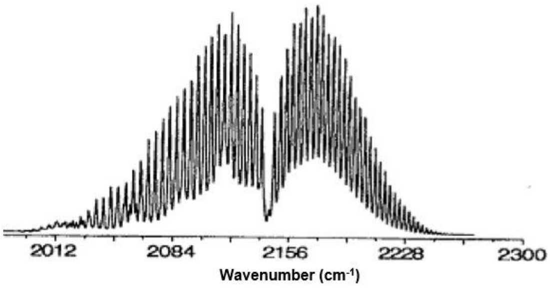

Fig. 2. The IR spectrum of carbon monoxide

From the measurement of the spacing between two adjacent lines, equal to 2B, it is possible to obtain the rotational constant; from this constant, knowing the masses of carbon and oxygen, the bond distance can be also obtained. This simple model explains the rotational spectrum of CO in an almost entirely qualitative way, so it is also suitable for secondary schools where little space is dedicated to physical chemistry. Molecules are not rigid rotators, but they vibrate around their bond position. Therefore, the next example concerns vibrations, and how IR spectroscopy uses them to identify the different types of chemical bonds, even in the presence of isotopic substitution.

3.1.2 The IR Spectrum of Chloroform

Chloroform and deuterated chloroform, penta-atomic molecules characterized by a pyramidal structure, have nine fundamental vibrational frequencies. A simplified model considers these

vibrations as independent harmonic oscillators. The solution of the corresponding Schrödinger equation allows us to determine the energy states of a harmonic oscillator according to the equation (1). Furthermore, the frequency $\tilde{\nu}$ is related to the speed of light c and to the square root of the ratio between the oscillator force constant k and the reduced molecular mass μ according to (4).
The stretching frequency of the C-H bond in chloroform is 3021 cm^{-1}; the stretching frequency of the C-D bond in deuterated chloroform is 2245 cm^{-1}. These values are related to the reduced masses: the ratio of the observed frequencies of the C-H and C-D bonds is almost equal to the square root of the inverse of the ratio of the reduced masses of the C-H and C-D bonds - where the reduced mass for chloroform is $m_C \times m_H / (m_C + m_H)$ and for deuterated chloroform is $m_C \times m_D / (m_C + m_D)$.
The data reported and relation (4) imply that the force constants in the two cases are equal; consequently, the force constant of the oscillator is a measure of the strength of the chemical bond between the two atoms, determined only by the interaction between the electrons of both; thus, it is not affected by the isotopic substitution.
In summary; the difference between $CHCl_3$ and $CDCl_3$ lies in the replacement of a hydrogen atom (H) with a deuterium atom (D). Deuterium has a significantly larger mass than hydrogen. The vibrational frequency of a bond is directly related to the reduced mass of the two bonded atoms. Deuterium is heavier than hydrogen, so the reduced mass of the C-D bond in $CDCl_3$ is greater than the reduced mass of the C-H bond in $CHCl_3$. Due to the increased reduced mass, the C-D bond in $CDCl_3$ vibrates at a lower frequency compared to the C-H bond in $CHCl_3$. This shift in vibrational frequency is directly observable in their respective IR spectra, while the strength of the chemical bond is not affected by isotopic substitution.
In conclusion, the vibrational frequency of the C-D bond predictably shifts due to the change in mass; this provides strong evidence for the quantization of vibrational energy. If vibrational energy were not quantized, the isotopic substitution would not have such a predictable and significant effect on the vibrational frequency. A similar example is possible by comparing the IR spectra of HCl and DCl molecules [9]. For further information suitable for secondary school, it is possible to refer to other sources [8].

3.2 Visible Spectroscopy

When a molecule absorbs UV or visible light, an electron within the molecule is excited from a lower energy molecular orbital to a higher energy molecular orbital. There are different types of transitions, such as $\sigma \rightarrow \sigma^*$, $n \rightarrow \pi^*$ or $\pi \rightarrow \pi^*$.
It is necessary to define some terms commonly used in UV-Vis spectrophotometry. Absorption spectra are characterized by the *transmittance T* at a given wavelength; this is defined by

$$T = I/I_o \qquad (5)$$

where I is the intensity of light transmitted by the sample and I_o is the intensity of light incident on the sample. When a cell is used for a sample in solution, I is taken to be the intensity of light transmitted by the cell, while I_o is taken to be the intensity of light transmitted by the cell filled with pure solvent. Another way of describing spectra is in terms of the *absorbance A,* where

$$A = \log I_o/I \qquad (6)$$

The absorbance *A* is related to the path length *d* of the sample and the concentration *c* of absorbing molecules by the Beer–Lambert law:

$$A = \varepsilon\, c\, d \qquad (7)$$

where *ε* is called the *molar absorption coefficient* when the concentration is expressed in moles per unit of volume. The quantity ε is an intrinsic property of the absorbing material that varies with wavelength in a characteristic manner; its value depends very slightly on the solvent used or on the temperature.
Absorption bands in the visible region of the spectrum correspond to transitions from the ground state of a molecule to an excited electronic state, that is 170 to 300 kJ mol^{-1} above the ground state. In many substances the lowest excited electronic state is more than 300 kJ mol^{-1} above the ground state and no visible spectrum is observed. Colored compounds absorb in the visible; they generally have some weakly bound or delocalized electrons such as the odd electron in a free radical or the p electrons in a conjugated organic molecule. It is possible to obtain useful information by the interpretation of visible spectra, for example the visible absorption spectrum of organic salts characterized by aromatic nitrogen-containing heterocycles linked by a polymethine bridge with conjugated double bonds [10]. The general formula of these compounds is represented in Figure 3, where Z = S, R = ethyl, n = number of ethylene units between rings. Since Z = S, these compounds are indicated as thiacyanine dyes.

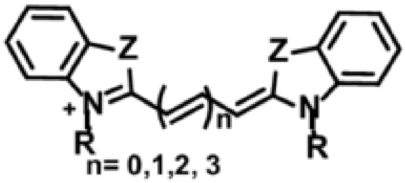

Fig. 3. General formula of thiacyanine dyes

The data obtained from visible spectroscopy are listed in Table 4, that reports the number of ethene units between rings, λ_{max}, and the molar absorption coefficient of the thiacyanine dyes considered.

n	***λ*** $\boldsymbol{\lambda_{max}}$ **(nm)**	***ε* (L / mol cm)**
0	423	8.5×10^4
1	557	1.5×10^5
2	650	2.3×10^5
3	758	2.5×10^5

Table 4. Number of ethene units, λ_{max}, and molar absorptivity of thiacyanine dyes.

The visible bands for polymethine dyes arise from electronic transitions involving the p electrons along the polymethine chain. The wavelength of these bands depends on the spacing of the electronic energy levels. These molecules can be treated theoretically using the "free electron" model. According to this model, the spectral characteristics in the visible region are determined solely by the π-electrons, which are "freely" in motion along the chain, with the sigma electrons localized between the connected atoms. Thus, the π-electrons of a conjugated dye molecule can be modeled using a one-dimensional "particle-in-a-box". The quantum mechanical solution for the energy levels of an electron placed in a one-dimensional box of length L is given by equation:

$$E_{(n)} = n^2h^2/8mL^2 \qquad (8)$$

where m is the mass of an electron and *h* is the Planck constant; the quantum number n may take integer values 0, 1, 2, 3, … The Pauli exclusion principle limits the number of electrons in each level to 2 with opposite spin (+1/2, -1/2). Therefore, if there are N π-electrons, the ground state of the molecule will have N/2 number of levels completely filled (if N is an even number). For a conjugated carbon chain with 6 π electrons, N = 6. When this conjugated system absorbs light, the valence electrons will be excited from the highest occupied molecular orbital (HOMO; n1 = N/2) to the lowest unoccupied molecular orbital (LUMO; n2 = N/2 + 1).

An orbital is a wave function for a single electron. The energy change for this electronic transition is:

$$\Delta E = (N+1)^2h^2/8mL^2 \qquad (9)$$

The measured energy separations for the upper and ground electronic states of thiacyanine dyes (Table 4) have been compared with the values calculated using the mentioned quantum model. The measured energy jumps for each value of n agree with the calculated values, providing evidence for quantized energy levels.

3.3 UV Spectroscopy

The electronic absorption spectrum of a molecule can be significantly influenced by the solvent in which it is dissolved. This phenomenon, known as solvatochromism, manifests as a shift in the position (and sometimes intensity) of the UV/Vis absorption band when the solvent polarity changes. Solvatochromism arises from interactions between the solute molecule and the surrounding solvent molecules, such as hydrogen bonding, ion-dipole forces, and dipole-dipole interactions. If these interactions preferentially stabilize either the molecule's ground state or its excited state during an electronic transition, a pronounced shift in the absorption band is observed. The shift in the UV absorption spectrum of acetone when dissolved in water compared to hexane is primarily due to solvent effects. Acetone exhibits a n → π* transition in the UV region. This involves the excitation of a non-bonding electron (n) on the oxygen atom of the carbonyl group to an antibonding π* orbital. Hexane is a nonpolar solvent, whereas water is a highly polar solvent with strong hydrogen bonding capabilities. Hydrogen bonds can be formed with the lone pair of electrons on the oxygen atom of acetone. This hydrogen bonding stabilizes the ground state of the acetone molecule. Therefore, to excite the electron to the π* orbital requires more energy in the presence of water. This results in a blue shift (shift to shorter wavelengths) of the absorption band compared to hexane (Figure 4).

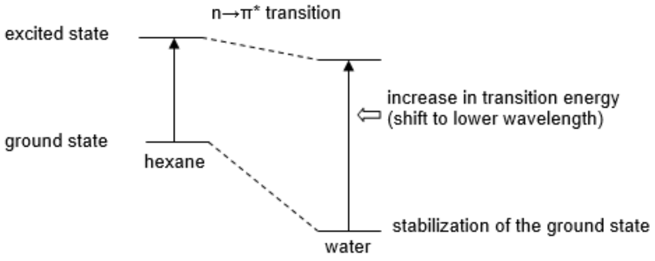

Fig. 4. The n → π* transition in hexane and in water.

In summary, the blue shift observed in the UV absorption spectrum of acetone in water compared to hexane is primarily due to the stabilization of the ground state of acetone by hydrogen bonding with water molecules. The energy jump is highlighted in Figure 5, which also shows the intermediate position of the absorption peak in propan-2-ol.

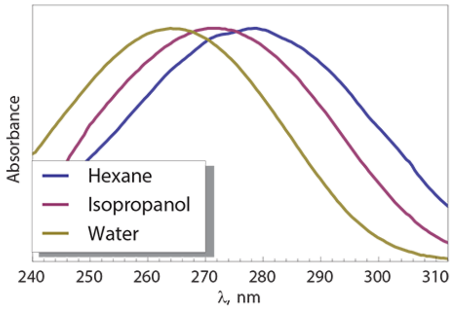

Fig. 5. Absorbance for acetone UV spectra: 279 nm in hexane, 264.5 nm in water, intermediate in propan-2-ol (referred to as isopropanol)

Therefore, UV spectroscopy can provide information on the energy of the hydrogen bond. In fact, from the energy difference between the two absorption peaks (in water and in hexane) it is possible to obtain, with the appropriate calculations, an energy difference equal to 24.7 kJ/mol, typical of the hydrogen bond.

While the shift in UV absorption itself doesn't directly "prove" quantization, it provides strong supporting evidence for the concept. It demonstrates that the energy levels involved in electronic transitions are sensitive to the molecular environment, and the observed shifts are consistent with the idea of discrete, quantized energy levels within the molecule.

Similarly, the case study related to retinol can provide the basis for the application of quantum mechanical principles in a biological context [11].

4. Conclusions

Compared to teachers in other countries, Italian science teachers consider the level of connection between chemistry and biology much higher than the level of connection between chemistry and physics [12]. The teachers' background could provide a possible explanation: in other countries, unlike Italy, degrees allowing for flexible science–teaching qualifications are available. In contrast, most Italian science teachers have a degree in biology or the natural sciences; science teachers with a strong background in chemistry are not common, and a degree in physics is not a suitable qualification to teach chemistry or biology in upper secondary school. As a result, the links between chemistry and physics that Italian teachers master are poor [12]. Therefore, instances and case studies discussed here have a particular formative value for Italian science teachers. The students involved in the project have shown increasing involvement year after year. Initially, the teacher explained some theoretical concepts, starting from atomic spectroscopy; subsequently, groupwork was organized for students to promote cooperative learning methods. Each group was assigned a different case study. Participation in the activities was high: students asked questions, advanced hypotheses, and drew conclusions guided by the teaching materials. The conceptual difficulties reported by the students from time to time have led to a progressive improvement of the work materials and a higher level of understanding, as evidenced by the final presentations produced by the students at each iteration of the project.

The evaluation criteria (Table 5) took into account: understanding of concepts (5 points out of 10), communication (3 points out of 10), teamwork (2 points out of 10). At the end of the first implementation, approximately 60% of students achieved a "very good" grade (points 8-9/10), 20% "excellent" (10/10), 20% "poor" or "very poor" (6/10 or < 6/10). In subsequent implementations, these percentages showed some fluctuations due to the different contexts, with a positive trend.

Evaluation criteria	**Understanding of concepts (5/10):** Ability to explain key scientific concepts clearly and accurately. Correct use of scientific terminology. Ability to connect concepts to concrete examples or practical applications. Ability to analyze data, graphs, or experiments.	**Rating scale from 1 to 10**	**Excellent (10):** In-depth understanding, critical analysis, effective communication, exemplary collaboration. **Very good (8-9):** Good understanding, accurate analysis, clear communication, effective collaboration. **Satisfactory (7):** Basic understanding, partial analysis, adequate communication, sufficient collaboration. **Poor (6):** Limited understanding, superficial analysis, unclear communication, insufficient collaboration. **Very poor (<6):** Lack of understanding, incorrect analysis, ineffective communication, lack of collaboration.
	Communication (3/10): Clarity and organization of the presentation. Effective use of visual aids (slides, graphs, etc.). Ability to answer questions clearly and concisely.		
	Teamwork (2/10): Fair distribution of tasks within the group. Ability to work collaboratively and respectfully.		

Table 5. Evaluation criteria and rating scale.

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