

CHEMISTRY

On the Possibility of Standardless Analysis of a Substance by Time-Resolved Spectroscopy in UV and Visible Regions

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The development of standardless quantitative analytical methods, i.e., methods that do not require the use of material standards (samples of standard composition), is topical primarily in relation to the problem of preparing standard samples, which is caused by a huge and permanently increasing number of known chemical compounds.

The general idea of using theoretical and experimental IR spectrometry for standardless quantitative molecular analysis was proposed and developed in [1-4]. It consists in determining the desired concentrations of compounds based on integrated absorbances of bands in measured IR absorption spectra being compared with calculated absolute intensities of these bands and the solution of corresponding sets of equations. A similar approach was developed for the methods of quantitative standardless analysis based on the spectra in UV and visible regions (vibronic spectra) [5]. Expected errors in the determination of concentration were estimated at $\leq 30\%$ for very small amounts of substance required for analysis (≤ 1 mg) and low concentrations of studied impurity molecules ($\leq 10^{-4}\%$).

Currently, vibronic spectroscopy shows the intensive development of methods for recording time-resolved spectra of complex molecules, which significantly expands analytical possibilities.

In this work, we first demonstrated the basic possibility of the standardless qualitative and quantitative analysis of complex substances by time-resolved vibronic spectroscopy in the UV and visible regions.

The main idea of the proposed approach is as follows. Let a studied compound be excited by an optical radiation pulse of intensity I_0 and rather short duration τ so that within this time molecules do not luminesce. After the end of the optical excitation event ($t \geq 0$), the emission spectrum of molecules of the compound $I(\omega, t)$ is recorded in sufficiently wide frequency and time ranges. The luminescence intensity $I(\omega, t)$ depends on transition probabilities w_{ij} and the initial (at $t = 0$) level population n_{0j} , which, in turn, depends on the concen-

tration of molecules C , the intensity I_0 (and duration τ) of the exciting radiation pulse, and transition probabilities; therefore, with the knowledge of the relative luminescence intensity $I(\omega, t)/I_0$, it is possible to determine (only from the experiment!) both these probabilities w_{ij} (and transition frequencies ω_{ij}) and the desired concentration of molecules C by solving the inverse spectral problem.

The time dependence of the luminescence spectrum is of significant importance in this method. Even for spectra in relative intensities, it is directly determined by transition probabilities and, hence, provides the determination of their absolute values and, consequently, the absolute values of concentration C without preliminary calculation of absolute intensities as in previously proposed standardless methods [1-5].

Let us consider this in more detail.

The spontaneous emission (fluorescence) intensity for the transition $l \rightarrow k$ is

$$I_k^{\text{em}}(\omega_k, t) = \hbar \omega_k w_{lk} n_l(t), \quad (1)$$

where the time dependence of the population of the l th level $n_l(t)$ is determined by the initial population of levels as a result of light absorption $n_l(0) = n_{0j}$ and by transition probabilities and can be found from the solution of a set of kinetic equations for populations $n_k(t) = \sum_j [\Phi(t)]_{lj} n_{0j}$. In the general case, elements of the

matrix $[\Phi(t)]$ are expressed as sums of exponential functions $\exp(-w_{pq}t)$, where $w_p = \sum_{q < p} w_{pq}$ are total probabilities of transitions from the p th state to all lower states. Coefficients of exponentials are determined by probabilities w_{pq} and, for $w_{p'q'} = w_{pq}$ ($p', q' \neq p, q$), additionally contain multipliers polynomial with respect to t .

The initial population n_{0j} after absorption depends on the concentration of molecules C , their relative thermal distribution over levels N_j before absorption (Boltzmann distribution), absorption probabilities w_{ij}^{abs} , and the intensity of exciting radiation $I_0(\omega_j, t)$ (spectral

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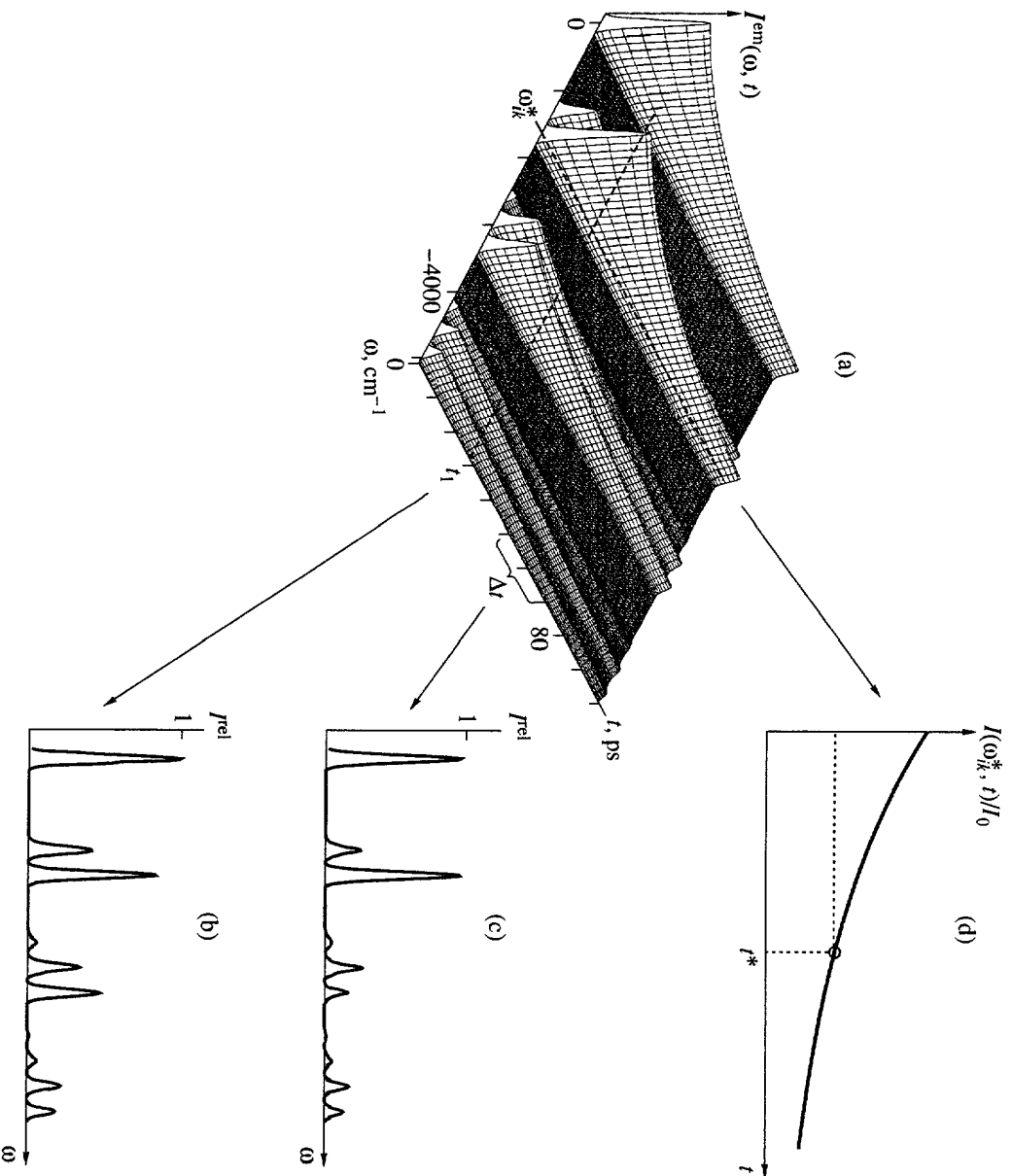


Fig. 1. (a) Multidimensional (time-resolved) luminescence spectrum of the butadiene molecule. (b) spectral curve for the fixed point in time t_1 , (c) integral spectral curve for the time Δt , and (d) spectral curve for the fixed frequency ω_{jk}^* .

composition and time shape of the pulse) and can be represented by the formula

$$n_{0j} = \frac{1}{c} \sum_l C \sum_l^{abs} N_l \int_0^t I_0(\omega_{lj}, t) dt, \quad (2)$$

where we assume that the pulse duration is much smaller than the lifetime of excited levels, so that fluorescence during excitation can be neglected. Without loss of the generality of consideration, we can assume that the pulse of exciting radiation is rectangular

$\int_0^t I_0(\omega_{lj}, t) dt = I_0(\omega_{lj})\tau$ with a narrow spectral composition corresponding to the resonance excitation of molecules to the n th state with the frequency ω_{0n} ; $I_0(\omega_{0j}) = I_0\delta(\omega_{0j} - \omega_{0n})$, and the temperature is sufficiently low

($T \approx 0$ K, which is typical, e.g., for a supersonic jet experiment), so that before light absorption all molecules are in the lowest (zero) state; $N_i = \delta_{i0}$ (δ_{ij} is the Kronecker symbol). Then, taking into account the relationship between the emission and absorption probabilities $\left(w_{jk} = \frac{h}{\pi c^3} \omega_{jk}^3 w_{ki}^{abs} \right)$, expression (1) is transformed to

$$\frac{I_{jk}^{em}(\omega_{jk}, t)}{I_0} = \frac{\pi C^2}{2} \tau C \omega_{jk} \omega_{0n}^{-3} w_{jk} w_{ni} n_0 I [\Phi(t)]_{jn}. \quad (3)$$

Relative intensities of the observed luminescence spectrum $I^{em}(\omega, t)/I_0$ explicitly depend on the concentration

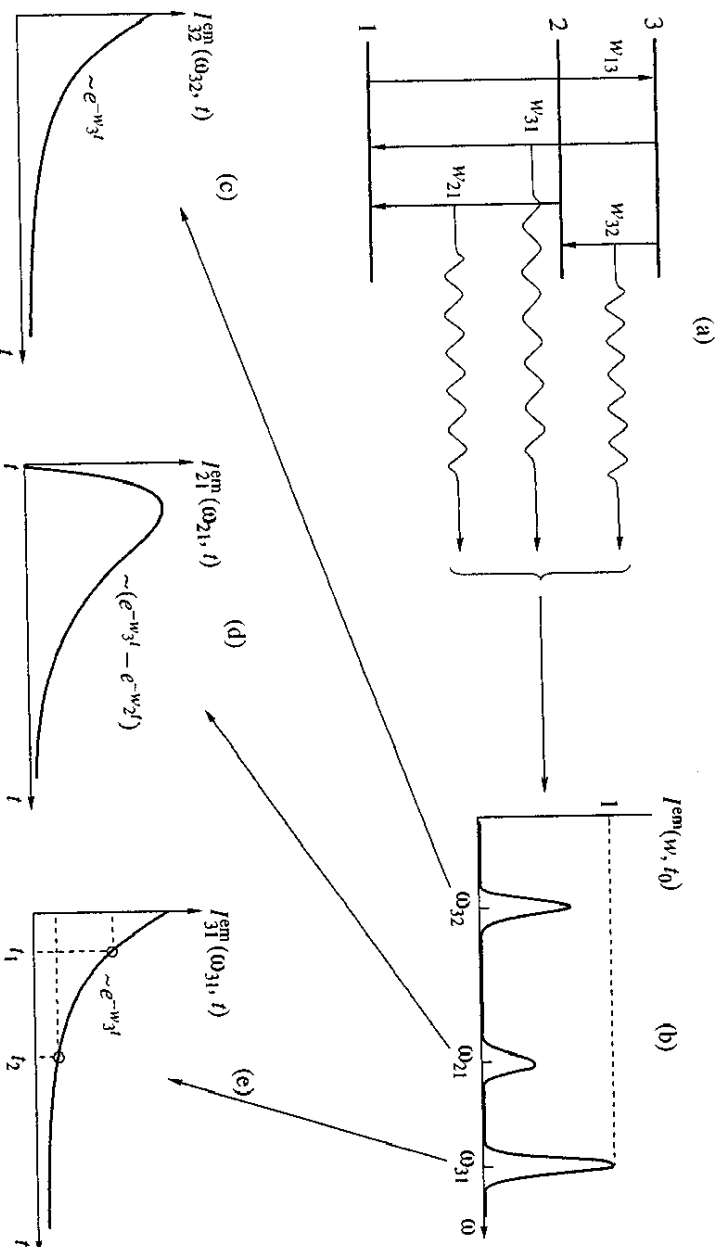


Fig. 2. Three-level model: (a) level system; (b) emission spectrum in the whole frequency range recorded at time t_0 ; and time dependences of line intensities corresponding to transitions (c) $3 \rightarrow 2$, (d) $2 \rightarrow 1$, and (e) $3 \rightarrow 1$.

of molecules C , which opens up the possibility of its determination from this spectrum. The structure of expression (3) makes it possible to solve the problem of the qualitative and quantitative spectrochemical analysis of a substance in two steps, which significantly simplifies the experiment. Indeed, it is possible to record relative line intensities (and transition frequencies) of the time-resolved emission spectrum (Fig. 1a) $I_{ik}^{em}(\omega_{ik}, t) \sim \omega_{ik} W_{ik} |\Phi(t)|_{in}$ and, from these experimental data, to determine frequencies and probabilities of vibronic transitions. Methods for solving these problems for time-independent vibrational and vibronic spectra (Figs. 1b, 1c) were developed in [6, 7] and can be easily extended for the case of time-resolved spectra. Obtained "experimental" values of transition frequencies and probabilities make it possible to pose and solve problems of the qualitative analysis of a substance using molecular simulation methods developed previously [6, 8] and to refine parameters of molecular models in the ground and excited states (geometry, force constants, etc.).

For determining the concentration of molecules C and, consequently, the implementation of quantitative standardless analysis, it is now sufficient to measure the relative intensity $I^{em}(\omega_{ik}, t)/I_0$ (3) for only one frequency ω_{ik}^* and point in time t^* rather than in all (or many) spectral and time intervals (Fig. 1d).

Thus, the proposed approach provides the qualitative and quantitative analysis of a substance without using samples of standard composition and barely implemented measurements of absolute integrated absorption and luminescence intensities.

This is the general concept of our approach. It can be most clearly illustrated with an example of a three-level model (Fig. 2). For the initial excitation to the state 3, the emission spectrum contains three lines corresponding to the transitions $3 \rightarrow 1$, $3 \rightarrow 2$, and $2 \rightarrow 1$ (Fig. 2b). The time dependences of their intensities are different; in particular, for the transition $2 \rightarrow 1$, the dependence is of biexponential form (Figs. 2c-2e):

$$\frac{I_{31}^{em}(\omega_{31}, t)}{I_0} = \frac{\pi C^2}{2} \tau C \omega_{31}^{-2} W_{31}^2 e^{-W_3 t}, \quad (4)$$

$$\frac{I_{32}^{em}(\omega_{32}, t)}{I_0} = \frac{\pi C^2}{2} \tau C \omega_{31}^{-3} \omega_{32} W_{31} W_{32} e^{-W_3 t}, \quad (5)$$

$$\frac{I_{21}^{em}(\omega_{21}, t)}{I_0} = \quad (6)$$

$$\begin{aligned} &= \frac{\pi C^2}{2} \tau C \omega_{31}^{-3} \omega_{21} \frac{W_{31} W_{21} W_{32}}{W_3 - W_2} (e^{-W_2 t} - e^{-W_3 t}), \\ &W_3 = W_{32} + W_{31}, \quad W_2 = W_{21}. \end{aligned} \quad (7)$$

Relative line intensities of the spectrum at the given t_0 give a set of equations for the determination of relative transition probabilities, e.g.,

$$\frac{W_{32}}{W_{31}} = \frac{\omega_{31} I_{32}^{em}(\omega_{32}, t_0)}{\omega_{32} I_{31}^{em}(\omega_{31}, t_0)}$$

Additional information of the time dependence of the spectrum makes it possible to determine the total probabilities, e.g., $W_3 = (t_2 - t_1) \ln \frac{I_{31}^{em}(t_1)}{I_{31}^{em}(t_2)}$, which, taking

into account expressions (7), makes the problem of absolute values of transition probabilities w_{ij} completely definite and easily solvable either directly or, in a more complex case of the multiexponential time dependence of the spectrum, by methods for solving inverse problems. This can be always done with a sufficient quantity of experimental data (relative intensities at different points in time).

This is the main and qualitatively new information provided by time-resolved spectra for analyzing complex molecules and their mixture in comparison with conventional spectra.

Concentration C is easily determined from relative fluorescence intensity (4)–(6) for known transition probabilities w_{ij} . For quantitative analysis, it is sufficient to record spectra not in the whole frequency range, but only in its part corresponding to transitions from one initially excited state $I_{31}^{em}(\omega_{31}, t)$ and $I_{32}^{em}(\omega_{32}, t)$ (see Figs. 2c, 2e) because intensities of these lines are independent of the characteristics of the transition 2 \rightarrow 1. This significantly simplifies the solution of inverse problems and the analysis because time dependences for all these lines are identical ($\exp(-w_3 t)$) and are determined by the total probability of transitions from state 3. This fact can also serve as a criterion for the selection of experimental lines in posing inverse problems (i.e., lines that correspond to another transition but fall into the given frequency range are excluded from consideration). Other parts of the full spectrum (in the given case, $I_{21}^{em}(\omega_{21}, t)$, see Figs. 2b, 2d) can be useful in qualitative analysis because they provide more complete information on the levels of the molecule and transition probabilities (ω_{21}, w_{21}).

Actual large molecules exhibit a complex system of vibronic energy levels and, from this standpoint, significantly differ from the simplest three-level models. However, to a good approximation for an appropriate experiment, the above results are also applicable to complex molecules.

Let a molecule be resonantly excited with a short radiation pulse to the second purely electronic ($v_j' = 0$) state. The fluorescence spectrum of the transition 2 \rightarrow 1 will involve vibrational structure ($0 \rightarrow v$) with a large number of lines with the intensities

$$\frac{I_{21,v}^{em}(\omega_{21,v}, t)}{I_0} = \frac{\pi C^2}{2} \tau C \omega_{21}^{-3}(\omega_{21,v}) W_{20-10} W_{20-1v} e^{-w_{21} t}, \quad (8)$$

where $\omega_{21v} = \omega_{21} - \sum_i^i \omega_i v_i$, ω_{v_i} and v_i are the frequency and quantum number of the i th vibration, respectively, w_{21} is the probability of the purely electronic transition with the frequency ω_{21} , $w_{20-1v} = w_{21} \langle 0|v\rangle^2$ are the probabilities of vibronic transitions 2, $0 \rightarrow 1$, and $v_i \langle 0|v\rangle^2$ are Franck-Condon factors. We assume that $\omega_{20-1v} \approx \omega_{21}$, which is a good (within 10%) approximation because for large molecules vibrational frequencies are smaller than frequencies of electronic transitions by an order of magnitude. In addition, changes in molecular structure on electronic excitation are rather small, and the most significant integrals $\langle v'|v\rangle$ are those for which changes in quantum numbers are no larger than 1; therefore, the total probability of the transition from state 2 is equal to the probability of the purely electronic transition w_{21} .

The time dependences of line intensities in the vibrational structure of the spectrum are identical, and the problem is quite analogous to the three-level model. Hence, it follows that vibrational transitions $v_1 \rightarrow v_2$ in the ground electronic state (IR spectrum) are insignificant and can be neglected in quantitative analysis.

For rarefied gases (intermolecular interactions and radiationless transitions can be neglected), the same result is obtained on the wide-band excitation of molecules.

Unlike rarefied gases, in sufficiently dense media (dense gases, liquids, etc.), intermolecular interactions can play an important role. Intermolecular interactions lead to the transfer of the internal energy of a vibrationally excited molecule to external (translationally) degrees of freedom with the transition of the molecule to a lower vibronic state and an increase in the temperature of the medium. In this case, the information contained in the emission spectra in relative intensities is insufficient for finding all necessary transition probabilities and determining the concentration C . This is due to the fact that in this experiment the fraction of absorbed energy that was converted to the thermal motion of molecules by radiationless transitions remains unknown. It is necessary either to measure absolute intensities, which is very complicated in practice, or to use an additional experiment that provides the determination of the fraction of energy converted to heat.

We will not enlarge upon this problem because it requires special consideration in detail (it will be the subject of a separate publication); however, note that the measurement of a change in the temperature of the medium as a result of light absorption and emission can be used as this additional experiment. Thus, the proposed approach to the standardless spectrochemical analysis of substances can be also used for rather dense

media along with rarefied gases. It also provides the possibility of experimentally determining radiationless transition probabilities and constructing comprehensive molecular models [9].

This approach can be easily extended to the case of multicomponent mixtures with concentrations C_1, C_2, \dots, C_N :

$$\frac{I_{ik}^{\text{cm}}(\omega_{ik}, t)}{I_0} = \frac{\pi c^2}{2} \tau \sum_{q=1}^N C_q W_{ik}^q(\omega_{ik}, t), \quad (9)$$

where $W_{ik}^q = \omega_{ik}^q (\omega_{0n}^q)^{-3} W_{ik}^q W_{n0}^q [\Phi(t)]_{in}^q$. In fine-structure spectra, intensities are normalized to the line intensity of one of the components of the mixture (q_0),

$$\frac{I_{ik}^{\text{cm}}(\omega_{ik}, t)}{I_0^{\text{cm}}(\omega_0, t_0)} = \frac{1}{\sum_{q=1}^N \frac{C_q}{C_{q_0}} W_{ik}^q(\omega_{ik}, t)}, \quad (10)$$

and depend on relative concentrations. Total probabilities w_i^q are determined from the time dependence of lines corresponding to the q th component of the mixture, $\frac{I_{ik}^{\text{cm}}(\omega_{ik}, t)}{I_0^{\text{cm}}(\omega_{ik}, t_2)} = \frac{W_{ik}^q(\omega_{ik}, t_1)}{W_{ik}^q(\omega_{ik}, t_2)}$, whereas relative transition probabilities $w_{ik}^q/w_{i_0k_0}^q$ and, consequently, absolute values of w_{ik}^q (because total w_i^q are known) are determined from relative line intensities in the vibrational structure of the spectrum corresponding to the q th component. Then, the ratio between line intensities of different components (10) yields relative concentrations $C_q^i = C_q^i/C_{q_0}$, and relative intensities (9) yield the value of C_{q_0} and, consequently, the absolute values of concentrations $C_q = C_q^i C_{q_0}$.

In the case of non-fine-structure spectra with overlapping lines of different components of the mixture, the time dependence of their intensity is of complex "multicomponent" character, $I^{\text{cm}}(t) \sim \sum_{q=1}^q A_q \exp(-W_q t)$. Nevertheless, with a sufficient number of experimental values $I^{\text{cm}}(t)$, all total probabilities w_q can be determined. The algorithm for solving the problem of the quantitative and qualitative analysis of a mixture is the same as for a fine-structure spectrum except that the sum over all components of the mixture must be taken in line intensities.

The above-considered demonstrated that a method for the standardless quantitative and qualitative analysis of complex compounds and their mixtures can be developed on the basis of time-resolved vibronic spectroscopy in the UV and visible regions. Among the main advantages of this approach compared to existing methods [1–5], we emphasize the following.

Under particular conditions, quantitative analysis can be completely transferred to the experimental basis without preliminary calculation of absolute intensities for molecular models corresponding to the test substance. Thus, this opens the possibility of the simultaneous quantitative and qualitative analysis of unknown compounds and their mixtures in one experiment.

The use of luminescence spectra significantly improves the sensitivity of standardless analysis and provides remote probing of media under study.

The method is the most efficient for rarefied gases, which can be easily attained in many important cases in practice (air impurities in the upper atmosphere, analysis of samples of substances in laboratory conditions, etc.).

With the use of an additional "temperature" experiment, the method also provides information on radiationless transitions, which is of great importance in the direct analysis of dense gases and in the simulation of intermolecular interactions [9].

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