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Ionisation of lanthanum monoxide molecules by two-step excitation

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Ionisation of lanthanum monoxide molecules by a two-step scheme, in which the first-step radiation transfers a molecule into an excited electronic state, and the second-step radiation excites the molecule to the ionisation potential, is proposed; this makes it possible to increase the ionisation signal in comparison with one-step excitation.

Laser-induced ionisation (LII) flame spectrometry is based on the detection of electric charges that result from the ionisation of atoms of the element to be determined due to resonance absorption of the laser radiation by these atoms.[1] Using this method, detection limits lower than those provided by other spectroscopic flame methods have been achieved for more than 35 elements, including rare-earth elements.[2] The analytical form of the elements determined by LII spectrometry is usually the atoms formed on heating a specimen to be analysed in a flame. The fraction of free atoms depends on the element nature, the temperature of the analytical zone, the flame composition and a number of other factors. Readily accessible low-temperature flames have been used in the majority of studies employing LII spectrometry. However, the efficiency of such flames for the determination of rare-earth elements due to the small fraction of free atoms formed is low. On the other hand, the concentration of molecules of rare-earth element monoxides in the flame is rather high. It therefore seems sensible to use such molecules as an analytical form. However, there is almost no published work dealing with this problem. Only one study is known[3] in which LII spectra of SrO, YO and LaO were obtained. The use of monoxide molecules as an analytical form in LII spectrometry was reported in a communication[4] dealing with phosphorus determination.

The unique potential for enhancing the sensitivity and selectivity of the LII method lies in the use of a two-step scheme for the excitation of atoms in a flame.[5] Two-step schemes have hardly ever been used for excitation of molecules.

Lanthanum was selected as the object of this study because of: i, the availability of spectral and thermodynamic data for its compounds in the literature and ii, the physical and chemical properties of rare-earth elements are rather similar and lanthanum is a typical representative of this family of elements. The purpose of this work was to find optimum two-step schemes for the excitation of lanthanum monoxide molecules.

The experimental set-up consists of a laser spectrometer based on an exciting excimer laser (Figure 1). The radiation of an excimer XeCl laser ($\lambda = 308$ nm, mean pulse energy 31 mJ, pulse repetition rate 10 Hz) was used for the excitation of two DL-mini dye lasers (ESTLA, Tartu, Estonia). The mean energy of the dye laser pulses was 0.58 mJ (coumarin-540A dye) and 0.64 mJ (coumarin-47 dye). The dye laser radiation was directed by a set of mirrors and prisms into the flame of a preliminary mixing burner and focused by lenses. A water-cooled cathode was located in the flame. A ground burner nozzle served as an anode. Weakly focused dye laser radiation (beam diameter 2.5 mm) was directed into the flame at a distance of 2.5 mm from the cathode and parallel to it. The maximum spatial coincidence of both rays (λ_1, λ_2) was striven for. Using a pneumatic nebuliser, the solutions studied were aspirated into a natural gas air flame. Continuous recording of the ionisation signal of the LaO molecule was started simultaneously with the start of the dye laser scan.

The ionisation signal was fed through a blocking capacitor to the input of a broad-band amplifier and then to a RIFF-016 gating integrator (Mozaika, Moscow). The digital signal from the integrator was read by a digital voltmeter and simultaneously recorded by a strip chart recorder. The burner and the cathode were protected from electromagnetic interference by a copper jacket.

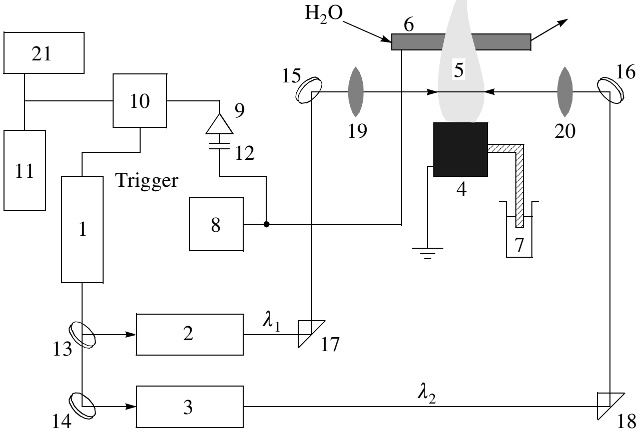

Figure 1 Block diagram for the experimental set-up: *1*, XeCl excimer laser; *2* and *3*, dye lasers; *4*, ground burner nozzle; *5*, flame; *6*, cooled cathode; *7*, analysed solution; *8*, high voltage power supply; *9*, broad-band preamplifier; *10*, RIFF-016 gating integrator; *11*, strip chart recorder; *12*, blocking capacitor; *13–16*, mirrors; *17* and *18*, rotating prisms; *19* and *20*, lenses; *21*, digital voltmeter.

A diagram of energy levels for the LaO molecule is presented in Figure 2. First, a spectrum of the LaO molecule was recorded at 535–565 nm (excitation by the first dye laser, coumarin-540A dye). The wavelengths corresponding to the $X^2\ ^+ \rightarrow B^2\ ^+$ transition (oscillator strength 0.16)[6] are known from the literature,[3] which made it possible to assign the observed bands. It is known from the same source that the excitation wavelength which we intended to use for second-step excitation also corresponds to the $X^2\ ^+ \rightarrow C^2\ _r$ transition (oscillator strength 0.21).[6] Therefore, in order to choose the wavelength for second-step excitation, the spectrum of the LaO molecule was recorded in the 440–470 nm range corresponding to this transition.

The spectrum is presented in Figure 3(*a*). The ionisation signal obtained from the transition at 440–470 nm is by one order of magnitude smaller than that at 535–565 nm. Since this observation contradicts the transition probabilities, it may be assumed that the molecules at the higher C^2 level more easily undergo collision deactivation than those at the $B^2\ ^+$ level.

In order to choose the second-step excitation wavelength, the spectrum of the LaO molecule was recorded in the 440–470 nm region with additional excitation by radiation with a wavelength of $\lambda = 561$ nm (this corresponds to the maximum signal in the 535–565 nm range, 0–0 band of the $X^2\ ^+ \rightarrow B^2\ ^+$ transition). The spectrum obtained with such two-step excitation is presented in Figure 3(*b*). The shapes of both spectra are almost similar, but the signal obtained from the radiation of two lasers is considerably stronger. The reason for this phenomenon is that with laser radiation wavelength of 561 nm, a strong ionisation signal is observed, which adds to the signal formed on excitation of a LaO molecule by the

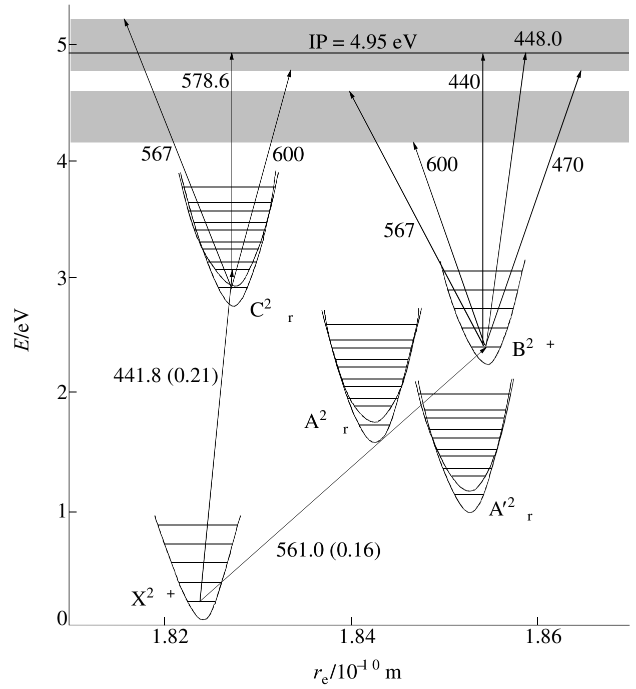

Figure 2 Simplified diagram of the energy levels of the LaO molecule. The numbers on the arrows indicate the wavelengths of the corresponding transitions in nm; the numbers in parentheses are the oscillator strengths of these transitions. The ranges of excitation energy scanned by laser radiation of the second excitation step are crosshatched.

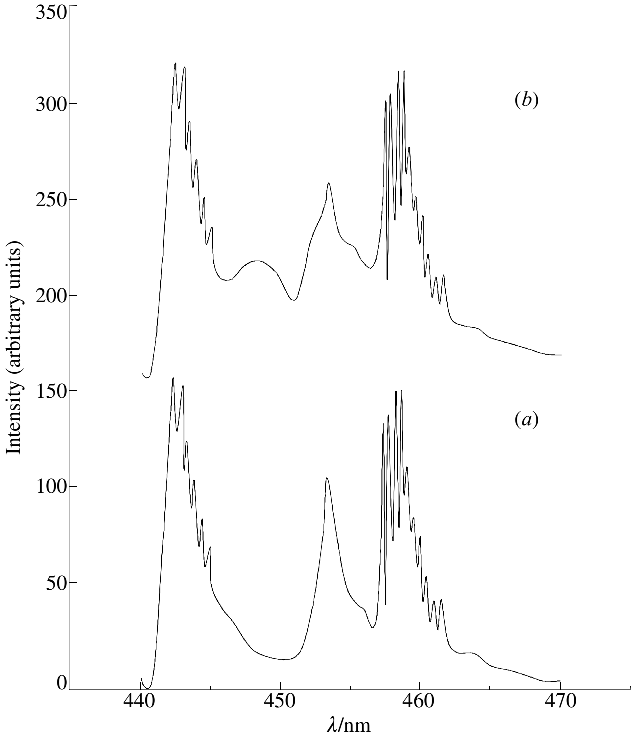

Figure 3 Molecular-ionisation spectrum of LaO molecule in the region of 440–470 nm: (*a*) using one dye laser; (*b*) with additional radiation of a second dye laser (561 nm).

second dye laser in the region of 440–470 nm. This simple addition of signals does not cause an enhancement typical of two-step schemes, when the signal is much stronger than the sum of signals resulting from each of the excitation steps. A comparison with the spectrum without first-step excitation [Figure 3(*a*)] makes it possible to determine the wavelength at which enhancement of the first-step signal occurs. This corresponds to an additional maximum in Figure 3 and equals 448 nm. In this case, the signal from first-step excitation ($\lambda = 561$ nm) increases by 25%. A simple consideration of the energy level structure for the LaO molecule shows that, within the error of wavelength measurement, the total excitation energy over the two steps equals the ionisation potential of the molecule and does not excite the molecule into any bound state. This is one of the reasons for the small signal enhancement in the second step.

Similarly, the spectrum of the LaO molecule was recorded in the region of 567–600 nm, also with additional excitation by radiation of $\lambda = 561$ nm. This did not result in any extra bands. Radiation of $\lambda = 441.8$ nm was then used as the first excitation step and radiation of $\lambda = 567$–600 nm was used in the second step. The wavelength at which signal enhancement occurs, determined from the spectrum obtained under these conditions, was found to be 578.6 nm. In this case, the signal from excitation in the first step only ($\lambda = 441.8$ nm) increases by 20%. As in the first case, the total excitation energy equals the ionisation potential of the molecule, within the error of wavelength measurement, and does not correspond to any bound state.

In order to enhance the ionisation signal, an attempt at direct photoionisation of the LaO molecule from the B^2 $^+$ excited state was made. For this purpose, part of the radiation from the exciting excimer laser ($\lambda = 308$ nm) with an energy of *ca.* 15 mJ was used as a photoionising step. The energy of the excimer laser quantum is sufficient for photoionisation of the B^2 $^+$ state. However, irradiation of the flame, even without focusing, gave an intense ionisation signal not related to the presence of lanthanum compounds in the flame.

The study performed revealed no excited states of the LaO molecule close to the ionisation potential (*ca.* 0.7 eV). Therefore, the use of two-step laser excitation schemes for ionisation of the LaO molecule does not give a considerable gain in the signal in comparison with the one-step scheme. The observed signal enhancement is explained by the fact that the total energy of the photons in the two excitation steps equals the ionisation potential of the lanthanum monoxide molecule. Since the cross-section of direct ionisation into the continuum is lower, the higher the photoelectron energy (*i.e.* the excess of excitation energy over the ionisation potential),[7] excitation of a molecule directly to the ionisation potential is most efficient. If higher intensity lasers are used for this purpose, the enhancement in such a two-step scheme is significant.

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