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Laser-Enhanced Molecular-Ionization Spectrometry of BaO and LuO in Low-Temperature Flame

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Abstract—The molecular ionization spectra of BaO and LuO were recorded in low-temperature natural gas–air flame with excitation laser wavelengths in the range 440–480 and 535–575 nm. Addition excitation of barium and lutetium monoxides by a second laser quantum did not amplify the ionization signal. One-step laser excitation with wavelengths of 549.3 and 466.2 nm is optimal for BaO and LuO, respectively.

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Laser-enhanced ionization spectrometry (LEI) is based on the laser excitation and subsequent ionization of atoms in flames. This method provides for ultralow detection limits (on the level of pg/mL and even fg/mL) for several tens of chemical elements [1]. The analytical form of elements for LEI spectrometry is atoms generated by the analyte sample upon introduction into the flame. The free-atom fraction depends on the element, analytical-zone temperature, and several other factors. However, certain elements (called refractory elements) in the low-temperature flames conventionally used in analytical spectrometry exist mainly as monoxide molecules. Either LEI does not determine such elements, or their detection limits are very high (tens of μg/mL and higher). One way to increase the sensitivity is to use higher temperature flames, such as an acetylene–nitrous oxide flame. The detection limits for refractory elements in these flames remain unsatisfactory, on the μg/mL level. The high temperatures of these flames increase the degree of ionization, thus decreasing the proportion of free atoms; increase noises due to the high concentrations of intrinsic flame ions; and shorten the lifetime of the detection electrode in the flame. Lastly, such flames are hazardous for operators. At the same time, the concentrations of monoxide molecules of refractory elements in the flame are rather high. Therefore, we designed a new method for the determination of chemical elements in flames in the form of molecules, namely, laser-enhanced molecular-ionization (MI) spectrometry. The underlying idea of this method is the ionization of laser-radiation-excited molecules and the detection of generated charges. This method achieves lower detection limits for refractory elements than high-temperature-flame ionization of their atoms, and under far milder conditions [2].

Systematic studies to develop laser-enhanced flame MI spectrometry started in the middle 1990s [3]. Two-step ionization schemes were proposed for rare-earth monoxide molecules [4, 5]: laser radiation first transfers a molecule to an excited electronic state and then to the ground state of the molecular ion whose energy corresponds to the ionization potential of the neutral molecule. As a result, the MI signal becomes several times stronger than in one-step excitation.

For laser-enhanced analytical molecular spectrometry to succeed, the structure of excited states and the pathways of dissociation, ionization, and deactivation of excited molecules should be known. An a priori choice of the optimal excitation scheme is impossible, because molecules, unlike atoms, have a great set of excited states for dissipating the excitation energy. Moreover, the radiation and energy characteristics for a great many molecules are lacking in the literature.

For some of the previously studied molecules (LaO, YO), the ionization potential E_i is lower than the dissociation energy D_0; therefore, the ionization probability for an excited molecule is higher than the dissociation probability. This situation is not a rule, as shown by analysis of the literature [6]. Many monoxide molecules have E_i far higher than D_0. As a result, the dissociation of a molecule during excitement becomes still more probable than ionization. For EuO and DyO molecules, for example, flame ionization spectra have not been recorded, but atomic lines were observed [7]. It is relevant to study this type of molecule, e.g., BaO (E_i = 6.46 eV [8], D_0 = 5.79 eV [6]) and LuO (E_i = 7.8 eV [9]; D_0 = 7.19 [6]).

This work studies the flame MI spectra of BaO and LuO and chooses optimal excitation schemes for these molecules.

EXPERIMENTAL

The setup used was a laser ionization spectrometer based on a xenon chloride excimer laser (λ = 308 nm; pulse energy, E_p = 45 mJ), which was used for pumping

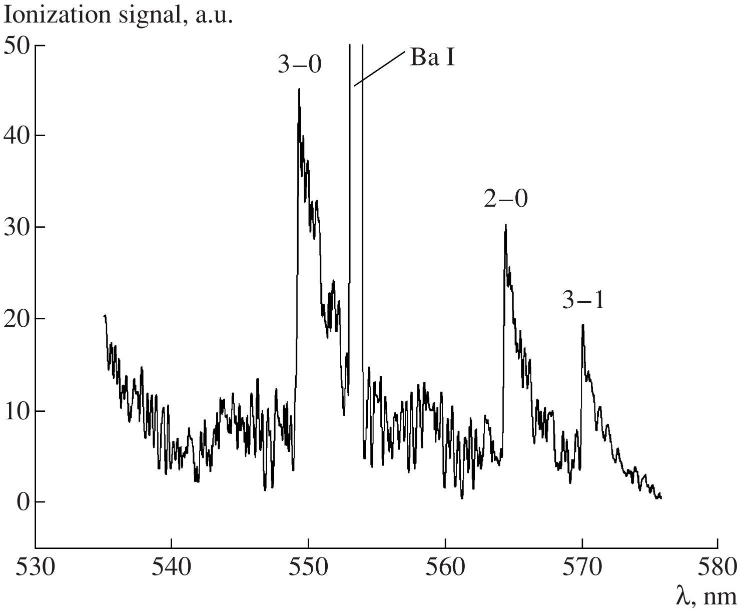

Fig. 1. BaO molecular ionization spectrum in the wavelength range 535–575 nm.

two frequency-tuned dye lasers: a Coumarin-153 laser (generation range, 535–575 nm) and a Coumarin-47 laser (generation range, 440–480 nm). The radiation of both dye lasers was directed into the natural gas–air flame, in which a cathode was placed with the potential 100–600 V relative to the grounded burner head. Analyte solutions were introduced into the flame by means of an pneumatic nebulizer. The ionization pulse signal was fed to a preamplifier and then measured with a gated integrator.

A 1-mg/mL barium solution was prepared from barium chloride (chemically pure grade), which was dissolved in 0.1 M HCl. A 1-mg/mL lutetium solution was prepared as follows. A 1.138-g sample of lutetium(III) oxide (pure for analysis) was dissolved under heating in 100 mL of 10% HCl (high purity grade), then transferred to a volumetric flask 1000 mL in capacity, and 0.1 M HCl was added to adjust the volume. Working solutions were prepared by consecutive dilution of the stock solutions with 0.1 M HCl.

RESULTS AND DISCUSSION

The BaO and LuO flame ionization spectra were recorded with laser excitation in wavelength ranges of 440–480 and 535–575 nm. Barium and lutetium solutions with the concentration of 1 and 20 μg/mL, respectively, were aspirated into flame. Figure 1 inhibits the ionization spectrum for a flame-atomized barium solution. The spectrum contains bands associated with the $A^1\Sigma^+$–$X^1\Sigma^+$ transition in a barium monoxide molecule with head wavelengths of 549.3 nm (3-0), 564.4 nm (2-0), and 570.1 nm (3-1). The maximum amplitude of the MI signal corresponds to 549.3 nm. The Ba I atomic line is clearly seen at 553.5 nm; its intensity is two orders of magnitude higher than the intensity of the molecular bands. The wavelengths found match the literature data [10, 11]. In the wavelength range 440–480 cm, a band with the wavelength 468.0 nm is observed with the intensity as low as 1.5 times that of the noise level.

Figure 2 displays the LuO molecular spectrum in the range 440–480 nm recorded for a lutetium solution aspirated into the flame. The spectrum contains a set of strong lines associated with the $B^2\Pi_{3/2}$–$X^2\Sigma^+$ transition in a lutetium monoxide molecule with head wavelengths of 466.2 nm (0-0), 467.2 nm (1-1), 468.4 nm (2-2), and 469.7 nm (3-3). The maximum amplitude of MI signals corresponds to the 0-0 band (466.2 nm). In the range 535–575 nm, two bands are observed due to the same transition in an LuO molecule with head wavelengths of 544.8 nm (3-4) and 546.4 nm (4-5). The latter have comparatively low intensities. Band assignment was performed with reference to [11]. For lutetium, there are no atomic lines in the spectrum, unlike in the ionization spectrum recorded with a barium salt introduced into the flame. Apparently, this is because of the higher stability of lutetium compounds (above all, lutetium monoxide) in flame. This correlates with the dissociation energy of monoxides.

For the two-step excitation of monoxide molecules, one dye laser was tuned to 549.3 and 466.2 nm for BaO and LuO, respectively. The wavelength of the other dye laser was tuned in the range 440–480 nm and 535–575 for BaO and LuO excitation, respectively. The signals corresponding to the excitation by the first and second dye lasers were separately subtracted from the signal excited by both dye lasers. This makes it possible to

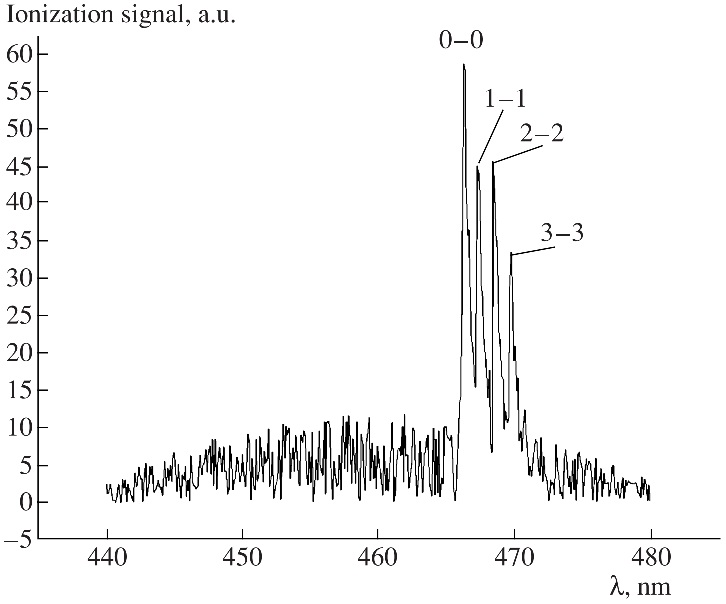

Fig. 2. LuO molecular ionization spectrum in the wavelength range 440–480 nm.

find the overall excitation energies of BaO and LuO molecules for which the sum of two individual signals is smaller than the signal excited by both lasers, i.e., for which signal amplification occurs. No such signal amplification is observed for either molecule studied.

For the excitation of BaO and LuO by the radiation of two lasers, the overall energy imparted to a molecule is 4.84–5.07 and 4.82–4.98 eV, respectively. Thus, the overall energy is substantially (by 1.39–1.62 and 2.82–2.98 eV, respectively) lower than the ionization potential in these molecules, making it impossible to implement two-step excitation schemes, unlike for molecules with lower ionization potentials [4, 5]. Evidently, the same pattern will be also observed for other molecules with high ionization potentials. Our results indicate a possible nonexistence of excited states of BaO and LuO molecules in the above-indicated energy ranges. Another possible reason is mixing of high-excitation molecular states due to collisions with other particles in the flame. The detection limits for barium in the atomic form and in the form of BaO calculated from the 3S criterium were 10 and 200 ng/mL, respectively; the lutetium detection limit was 250 ng/mL. Based on our studies of the laser-enhanced ionization spectra of BaO and LuO, we propose optimal one-step laser excitation schemes with the wavelengths 549.3 and 466.2 nm for BaO and LuO, respectively.

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