

Shift of chemical equilibrium of solutions by resonant IR laser radiation

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A shift of the chemical equilibrium was experimentally observed following nonresonant action of CO₂-laser radiation on the interface between organic and aqueous solutions of uranyl nitrate.

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It is known that in the gas phase selective excitation of molecule vibrations leads to a selective course of chemical reactions.^[1] In condensed media, an abrupt increase in the relaxation rate impedes an effective manifestation of selective excitation of the molecules.

It is shown in this paper that laser irradiation of the interface between two solutions leads, in vibrational excitation of stable complexes, to a shift of the chemical equilibrium.

The experiment was performed with a pulsed atmospheric-pressure CO₂ laser with pulse energy 2-3 J, pulse duration at half-height 200 nsec, and emission wavelength 944 cm⁻¹.^[2] By placing in the cavity a cell with BCl₃ gas at atmospheric pressure, it was possible to tune the laser with practically no energy loss to the wavelength 1040 cm⁻¹. The radiation pulse repetition frequency was 1 Hz.

The object of the investigation was the complex compound produced when uranyl nitrate is extracted with tributyl phosphate (TBF).^[2] The antisymmetrical valent vibration ν_3 of the uranyl exhibits in this complex resonant absorption at the frequency 945 cm⁻¹. The ester groups of TBF are characterized by intense absorption at 1040 cm⁻¹.^[4] It is known that the uranyl grouping is linear or almost linear, and that the axial ($0 = u = 0$) and equatorial bonds in the uranyl complexes are mutually-dependent.^[4,5]

The uranium was extracted from the aqueous solution by the tributyl phosphate through the action of laser radiation, in a flow-through regime. The results of the experiments are summarized in the table.

In experiments 1-4 we irradiated a thin layer of extractant flowing over the surface of the aqueous solution, and in experiment 5 we irradiated a thin layer of aqueous solution flowing over the extractant.

The quantitative analysis was by chemical titration with accuracy $\pm 2.5\%$. No increase in the temperature of the liquids was observed in the course of the irradiation. Special experiments performed without laser irradiation have shown that a temperature rise affects adversely the extraction of uranium with TBF. The extraction properties of the irradiated TBF solutions were preserved after re-extraction.

The presented data show that CO₂-laser radiation

improves the extraction of uranium with tributyl phosphate, if the radiation is incident on the interface through the organic phase. The absence of this effect when the radiation is incident through the aqueous phase is due to the strong absorption of the radiation by the water.

The observed shift of the chemical equilibrium on the interface between organic and aqueous solutions following resonant action of laser radiation on the complex comprising TBF and uranyl nitrate can be attributed to a strengthening of the equatorial bonds of the complex when antisymmetrical valence vibrations of the axial bond of the uranyl grouping of the complex are excited, and to the relative stability of the strengthened state, which is the factor causing the change in the conditions of the extraction equilibrium. The chemical-potential change that is thus produced upon selective absorption of the chemical potential leads to selective activation of the process of chemical sorption.

It should be noted that the absorption frequencies of uranyl complexes having different isotopic compositions differ somewhat. One can therefore regard the laser-extraction method as being worthy of attention as a possible method of isotope enrichment.

We have thus observed a nonthermal effect of IR laser

Experiment number	Equilibrium content of the uranium in the aqueous phase (g. liter)		Uranium distribution coefficient (K_D)		change of K_D of uranium, %
	prior to irradiation	after irradiation	prior to irradiation	after irradiation	
1	0.367	0.333	1.46	1.71	17
2	0.329	0.292	1.78	2.20	23
3	0.045	0.023	19.00	38.20	101
4	0.329	0.309	1.78	1.91	8
5	0.252	0.257	1.59	1.55	-2

1. Extractant 0.1 m solution of TBF in *n*-octane, initial aqueous solution—0.902 g/l of uranium in 4n HNO₃, irradiation at 944 cm⁻¹.
2. Extractant 0.1 m solution of TBF in kerosene, initial aqueous solution—the same, irradiation at 944 cm⁻¹.
3. Extractant 30% solution of TBF in kerosene, initial aqueous solution—the same, irradiation at 944 cm⁻¹.
4. Extractant 0.1 m solution TBF in kerosene, initial aqueous solution—the same, irradiation at 1043 cm⁻¹.
5. Extractant 0.1 m solution of TBF in CCl₄, initial aqueous solution—0.654 g/l of uranium in 4n HNO₃, irradiation at 944 cm⁻¹.

radiation on the chemical equilibrium in extraction systems, and have demonstrated the possibility of stimulating extraction processes by selective action of IR radiation both on the extracted components and on the extractant.

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