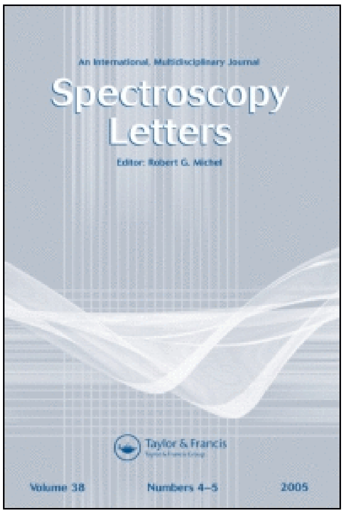

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Prospects of Dye Laser Applications to the Selective Laser Photophysics

V. S. Letokhov[a]
[a] Academy of Sciences USSR, Institute of Spectroscopy, Academgorodok, USSR

To cite this Article Letokhov, V. S.(1975) 'Prospects of Dye Laser Applications to the Selective Laser Photophysics', Spectroscopy Letters, 8: 9, 697 — 709

To link to this Article: DOI: 10.1080/00387017508067374

URL: http://dx.doi.org/10.1080/00387017508067374

SPECTROSCOPY LETTERS, 8(9), 697-709 (1975)

PROSPECTS OF DYE LASER APPLICATIONS TO THE SELECTIVE LASER PHOTOPHYSICS.

V.S.Letokhov

(Institute of Spectroscopy, Academy of Sciences USSR, Moscow, Podolskii rayon, Academgorodok, 142092, USSR)

ABSTRACT

Applications of tunable dye lasers in the process of selective atomic ionization have been considered for the purpose of laser isotope separation and substance purification.

INTRODUCTION. Generation of monochromatic radiation at any given frequency in visible and UV range is the most valuable feature of dye lasers, that makes them an extremely efficient instrument for selective action on a substance by laser radiation. Selective action means a selective excitation of atoms (molecules) of a particular sort which with the use of subsequent photophysical and photochemical processes makes it possible to separate atoms (molecules) of the selected sort from a mixture. The term "a sort of atom" means that any atom has a certain atomic number, a certain isotopic composition and, in principle, a certain quantum state of its nucleus. Such consecutive differences in atoms are due to the absolute difference in absorption spectra of all elements in the periodic table, as well as to the fact that atomic spectra have a clearly defined isotope structure and a hyperfine nuclear structure. Thus, selective action upon atoms by laser radiation is in essence laser separation of chemical elements, isotopes and nuclear isomers.

There may be a fairly great number of potential methods and schemes of selective action on atoms and molecules by laser radiation in UV, visible and IR range. These methods may employ both photophysical and photochemical principles (see reviews /1, 2/). Dye lasers oscillating in visible and UV range are best suited in excitation of electronic states of atoms and molecules, that is to be applied in the selective electronic photophysics and photochemistry. In the present paper consideration is given to prospects of tunable dye laser application to the selective atomic photophysics, that is to ways of their use in selective ionization of atoms by laser radiation which is, apparently, the most universal method of selective photophysics.

The method of selective atomic ionization by laser radiation was first put forward and realized back in 1971 on Rb-atoms /3/ and then presented in more detail in work /4/. Now, in view of the problem of laser isotope separation /5/, it is under wide discussion. In our opinion, the potentialities of the method of selective atomic ionization are beyond the scope of the problem. The method is quite appropriate specifically in separating atoms different elements to obtain particularly pure substances,and even in separating nuclear isomers to purify radio-active substances and setting up an active medium for nuclear γ-laser /6/. Dye lasers will have, in our opinion, a dominant role in realizing all these ways in practice.

SELECTIVE ATOMIC EXCITATION. Selective excitation is the first step in any process for selective action by laser radiation on atoms of a particular sort. Let's classify tuning, power and monochromatic requirements for laser radiation.

Fig. 1 shows energy distribution of allowed transitions from the ground state to the first excited one for 91 elements, from H to Am. Over one-half elements (53) can be excited just by dye laser radiation in the completely developed region from 12000 Å to 3500 Å. Using the radiation of the second harmonic in the well studied region down to 2500 Å we may excite 73 elements, that is 80% of all elements. In the region under development at present, from 2000 Å to 2500 Å, there are absorption lines of three elements only (Be,Te,B) and, at last,in the inaccessible region shorter than 2000 Å there are 16 elements which are listed in Fig.1. Thus, dye lasers are capable of excitation of all heavy elements, almost all middle-atomic-weight elements and unusable in exciting some 10 light-weight elements.

For the resonance transition 1-2 from the ground state "1" to an excited one "2" to be saturated by continuous wave, that is for almost one-half atoms to be kept excited

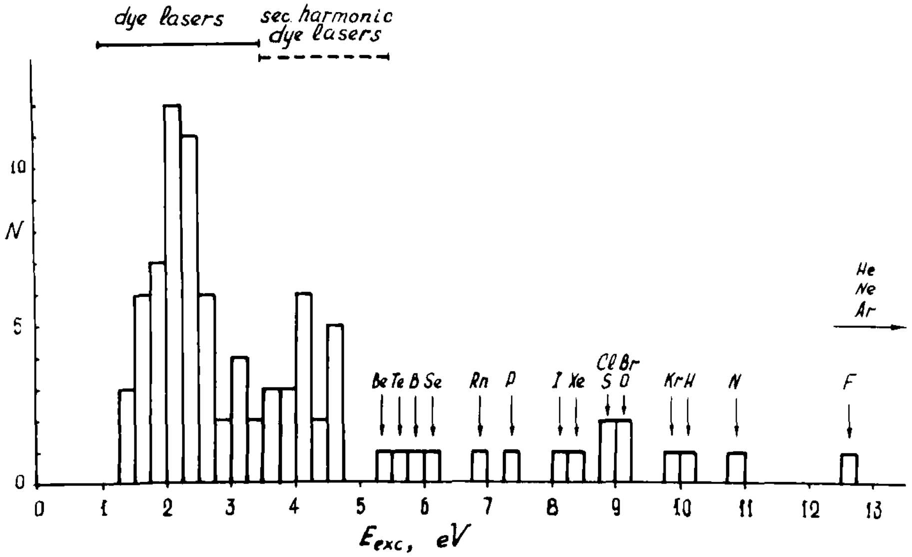

Fig. 1. Energy distribution of allowed atomic transitions for various elements (from H to Am) from the ground to the first excited state.

steadily, the power of the exciting radiation P_e should comply with the condition:

$$P_e \gtrsim \mathcal{P}_e = \frac{\hbar\omega_1}{2\sigma_e\tau}\,, \tag{1}$$

where $\hbar\omega_1$ is the energy of transition, σ_e is the cross-section of radiative transition, τ is the relaxation time of excited level population. In case the relaxation time is determined only by radiation decay to the ground state, i.e. $\tau = A_{21}^{-1}$, the saturation power doesn't depend on the level life time:

$$\mathcal{P}_e = \pi \frac{g_1}{g_2} \frac{\hbar\omega_1}{\lambda_1^2} \Delta\omega \tag{2}$$

For a typical atomic transition with the energy $E_e = 3$ eV and the Doppler width of absorption line $\Delta\omega == 3.10^{-6}\,\omega_o$ the saturation power $\mathcal{P} \simeq 10$ W/Cm^2.

For almost one-half atoms to be excited by a radiation pulse with the duration $\tau_p \ll \tau$, it is necessary that the pulse energy density $E_e\,(J/cm^2)$ should comply with the condition:

$$E_e \gtrsim \mathcal{E}_e = \frac{\hbar\omega_1}{2\sigma_e}\,, \tag{3}$$

where $\mathcal{E}_e$ is the saturation energy. For this typical atomic transition with $\tau = A_{21}^{-1} = 10^{-8}$ sec the cross-section will be $\sigma_e = 3.10^{-13}$ cm^2 and the saturation energy $\mathcal{E}_e = 10^{-6}$J/cm^2.

For efficient population of the excited level power and energy values of the order of $\mathcal{P}_e$ and $\mathcal{E}_e$ should be attained within a narrow spectral band $\Delta\lambda = 3\,.10^{-6}\lambda_o = 10^{-2}$ Å.

<u>IONIZATION OF EXCITED ATOMS</u> Selectively excited atoms may be photoionized by an additional radiation with the quantum energy $\hbar\omega_2 > E_i - \hbar\omega_1$, but $\hbar\omega_2 < E_i$. The wanted wavelength of radiation falls also in the region accessible for dye lasers. Fig. 2 shows the distribution of the energy essential to photoionize atoms of various elements from the first excited state providing this state is connected to the ground state by a radiation transition. In the region $\lambda < 2500$ Å, which is inaccessible for dye lasers and the second harmonic of their radiation, there are just some elements. Since these elements are not overlapped by those listed in Fig. 1 they may be photoionized by a laser radia-

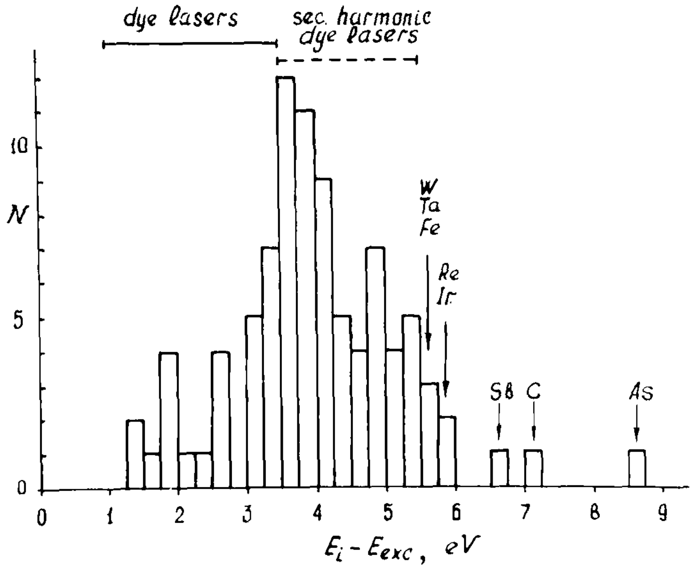

Fig. 2. Distribution of the energy required to photoionize atoms of various elements (from H to Am) from the first excited state.

tion with $\lambda > 2500$ Å provided the intermediate level energy is chosen properly.

To photoionize each excited atom at a rate competing with the rate of atomic relaxation to the ground state it is necessary that the power of photoionizing radiation should comply with the condition similar to (1):

$$P_i \gtrsim \mathcal{P}_i = \frac{\hbar\omega_2}{\sigma_i \tau} = \frac{\hbar\omega_2}{\hbar\omega_1}\,\frac{\sigma_e}{\sigma_i}\,2\mathcal{P}_e, \qquad (4)$$

where σ_i is the photoionization cross-section of excited atom. Thus, the photoionization of all excited atoms requires a power which exceeds that of exciting radiation in the ratio $(2\sigma_e/\sigma_i)$ approximately. Since the typical value of

$\sigma_i \simeq 10^{-17} - 10^{-18}$ cm^2 /7/ the P_i value in the case should make up $10^5 - 10^6$ W/cm^2, which is practically inaccessible. The use of an intermediate metastable level reduces requirements on P_i, but it is difficult to attain $\tau > 10^{-5}$ sec because of the short time of atoms flight through the light beam limited in diameter. Therefore in any case of non-resonance photoionization of excited atoms $P_i > 10^4$ W/cm^2.

Excited atoms may be ionized by a short radiation pulse synchronized with a short excitation pulse and with its duration being below the relaxation time τ. In this case, for the main portion of excited atoms to be photoionized, the pulse energy density E_i must obey the condition:

$$E_i \gtrsim \mathcal{E}_i = \frac{\hbar\omega_2}{\sigma_i} \qquad (5)$$

With $\hbar\omega_2 = 4$ eV and $\sigma_i = 10^{-17}$ cm^2 the wanted density of pulse energy $\mathcal{E}_i \simeq 0.1$ J/cm^2 in a time shorter than τ.

The use of autoionization resonances is the most drastic method for increasing the photoionization cross-section and for reducing requirements on power and energy of ionizing radiation. To cite an example, in the spectrum of Mg I from the excited state $3s3p\,{}^1P_1^o$ exist autoionization resonances with $\sigma_i = 5\cdot10^{-16}$ cm^2 /8/. Autoionization levels similar to these are known in spectra of Cu, Ag, Zn, Cd, Hg and other atoms. When employing an autoionization transition with its cross-section $\sigma_i = 10^{-14}$ cm^2 and an intermediate level with $\tau = 10^{-6}$ sec, the wanted power of ionizing radiation decreases to 10^2 W/cm^2.

The possibilities of such a resonance photoionization will be widened, when using autoionization of discrete levels arising below the ionization limit under external electric field. The electric field changes the electronic spectrum of atom so that some levels of discrete spectrum next to the ionization limit fall within the continuum and the rest become autoionized. The probability of their ionization decay rises rapidly with increase in the main quantum number. The optimum case is when the second laser radiation excites an atom to a state with the autoionization rate being higher than that of radiation decay but autoionization broadening less than the Doppler line width of the intermediate-autoionization state transition. In this case each excited atom will be ionized, the cross-sections of such an ionization approaching that of resonance transition between discrete energy levels. In this optimum case $\mathcal{P}_i \sim \frac{\hbar\omega_2}{\hbar\omega_1} \mathcal{P}_e \simeq 10-10^2$ W/cm^2, no matter what the intermediate level lifetime τ is. The calculations made in work /9/ show that this method can be realized in comparatively weak electric fields (no more than 30 kV/cm) which cause no electric breakdown in the irradiated atomic beam.

Selective atomic ionization with use of autoionization states (spontaneous or induced by external electric field) necessitates tunable radiation. And again dye solution lasers are best suited to this purpose.

APPLICATIONS OF THE SELECTIVE IONIZATION METHOD.

Most efficiently and well chosen scheme of selective atomic photoionization under the action of two (or more, in principle) laser beams with specifically tuned frequencies makes possible the ionization of each atom in the time

$\tau = 10^{-6} - 10^{-7}$ sec with the radiation power at each frequency being about 10^2 W/cm^2. When the radiation energy is completely spent on the atomic photoionization with $E_i \simeq$ 7-8 eV and the light beam cross-section of 1 cm^2 this corresponds to about 1/2 gram-atom of a substance ionized selectively per hour. Thus, a laboratory setup is capable, in principle, to separate about 1 ton of a substance in a year. Therefore the method of selective atomic ionization in combination with tunable 10 -100 W output power dye lasers tecnique may be considered as a rather efficient method of fine separation of substances at atomic level, i.e. laser atomic-molecular technology of materials.

The preparation of a substance in the atomic gaseous state is the first imperative step in this method. Most elements must be heated to rather high temperatures in this case. It is possible also to obtain atoms by decomposing molecular compounds. In the both cases we can act by laser radiation on a condensed medium or molecular gas to obtain atoms. For ions to be brought out of the atomic vapour, the use of a geometry, in which the atomic gas represents a beam of atoms, is more rational.

There are at least two promising large scale applications of laser technology at atomic level: isotope separation and substance purification (production of extremely pure materials).

LASER ISOTOPE SEPARATION by the selective ionization method, suggested for this purpose back in work /3/, has been considered in many papers /4,5,10/ and must be currently under extensive studies. Therefore we'll limit ourselves here to listing the requirements on dye lasers placed by this application. For this purpose it is necessary to have available dye lasers at wavelengths ranging from 6000 to 3000 Å with their bandwidth of no more than 0.01 Å and with the same stability of oscillation wavelength. The following two regimes are optimum: pulsed regime with a high repetition rate and CW one. Under the pulsed regime the peak power must make up $10-10^3$W/cm^2 with a repetition frequency of 10^3-10^4 Hz and a pulse duration of $10^{-8}-10^{-7}$ sec. Under the CW operation the power must amount to 10-100 W/cm^2 .The total power of radiation depends on the desired capacity of setup. To produce about one ton of final product per year it is necessary to have lasers with the mean power of the order of 10^2 W or more.

LASER PURIFICATION OF SUBSTANCE by the selective ionization method is no different from isotope separation in the principle of operation but necessitates a higher coefficient of separation (enrichment) within one step, over 10^3, say. This is quite practicable,since when atoms of different elements are separated there is no resonance charge transfer that limits the selectivity of the isotope separation method. Such a method has a number of substantial advantages against existing methods of substance purification based on the difference between specific chemical and physical properties of substance under purification and impurities.

Firstly, the method has an extremely high selectivity. The degree of purification, as the desired element is cleaned of any impurity, is no less than 10^3. This value depends on transfer of charge arising when an ion of the desired element comes into collision with a neutral atom of the impurity. In principle, by reducing the atomic density in the beam we may attain a separation selectivity of about 10^6, the efficiency therewith drops respectively. For example, should a commercial material with its purity of 10^{-7} % is taken for purification it may then be cleaned up to 10^{-10}% by the method of selective atomic ionization.

Secondly, the method is very universal. Any element (apart from some those listed in Fig.1), no matter what its physical and chemical properties (temperatures of fusing, boiling, reactivity, etc. is) can be selectively ionized by selecting frequencies of tunable dye lasers.

If there is a substance to be cleaned of one or more specified elements it is possible in this case to ionize selectively only impurities and to remove them from the atomic beam of the substance. Under these conditions the efficiency of the method is maximum while expenditures of light energy are minimum.

Thirdly, the method is rather adaptable for direct producing substances in the form of films as well asthose of complex composition. The ion beam may be directed over the surface of the substratum to produce a pure film. Independent selective ionization of two or three different elements at a time in different beams and collection of their ions on the same substratum seems to be feasible. Thus,it is possible to obtain films of complex atomic compounds and to control their composition by intensity of ionic currents.

The whole process of selective atomic ionisation, ion extraction from a beam and their deposition on the substratum may be accomplished in a high vacuum. It doesn't necessitate a contact between the substance under purification and any reagent or material, except for a substratum for which any material without unwanted impurities may be used.

The development of dye lasers of visible and UV range with tunable and controlled frequency, with a high mean power and a long service time form the basis for successful elaboration of the method. Laboratory experiments require average powers of 1-10 W, while pilot industrial setup will consume 10^2-10^3 W. These will be CW or pulsed lasers with a repetition pulse rate of about 10 kHz and over.

So, dye tunable lasers hold much promise for development and elaboration of new techniques of substance separation at atomic level. At the same time the potentialities described above will be practically realized only with the further advancement of tunable dye lasers, their average power being by 2-3 orders higher than that achieved at present.

REFERENCES

1. V.S.Letokhov. Science, 180, 451, 1973.
2. C.B.Moore. Accounts Chem. Res., 6, 323, 1973.
3. R.V.Ambartzumian, V.P.Kalinin, V.S.Letokhov. JETP Letters, 13, 305, 1971.

4. R.V.Ambartsumian, V.S.Letokhov. IEEE Journal Quant. Electr., QE-7, 305, 1971; Appl. Optics, 11, 354, 1972.

5. B.Snavely. Invited paper on VIII Intern. Quant. Electr. Conf., 10-13 June 1974,San-Francisco, USA.

6. V.S.Letokhov. JETP, 64, 1555, 1973; Optics Comm., 7, 59, 1973.

7. G.Marr. Photoionization Processes in Gases. Acad. Press, N.Y., 1967.

8. D.J.Bradley, P.Ewart, J.V.Nicholas, J.R.D.Shaw, D.G.Thompson. Phys. Rev. Letters, 31, 263, 1973.

9. L.N.Ivanov,V.S.Letokhov. Quantum Electronics, 2, 585,1975.

10.R.Levy,G.S.Janes. US Patent N 3772 519, 1970.