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Laser isotope separation †

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PART I.

I. History. Classification of Methods. Short Abstract of Review.

Considerable progress has been achieved recently in widening the region of laser wavelengths, in methods of tuning and in control over and stabilization of laser radiation frequency. This has opened the way for systematic study of rather delicate applications of laser light, where laser radiation acts on a substance selectively. Basically, the question is in development of the next stage of laser light applications which necessitate a higher degree of control over laser characteristics. The problem of selective action of laser radiation on a substance is of primary importance for an active use of coherent light in chemistry, especially in photochemistry, nuclear chemistry and biology. When lasers are used for isotope separation it becomes of special interest because in this case a serious influence of quantum electronics on nuclear engineering and nuclear power energetics becomes possible and the problem oversteps the limits of scientific employment of lasers. This field of laser radiation application places heavy demands on lasers and should stimulate their development to a certain degree. It has been just because of this we make an attempt to review the problem of laser isotope separation in this journal.

The idea to use an optic radiation for selective excitation of atoms and molecules with their particular composition and for subsequent photochemical isotope separation sprang up very long ago. It was born just after isotopes and the isotopic effect in atomic and molecular spectra had been discovered /1/. The first attempt to conduct photochemical separation of isotopes was made in 1922 in work /2/, where Cl_2^{37} molecules mixed with H_2 were excited by white light that passed through a filter containing mainly Cl_2^{35} molecules. The first successful experiment was conducted only after ten years by Kuhn and Martin /3/ though, who excited phosgene ($COCl_2^{35}$) molecules by the line 2816.18 Å of an aluminium spark. At that time Mrozovsky /4/ suggested that a specific isotope of Hg in the natural mixture should be excited selectively by the radiation of the line 2537 Å of Hg having passed through a resonant-absorbing filter (Mrozovsky filter) and the photochemical reaction between excited atoms of mercury and oxygen should be observed. A photochemical separation of mercury isotopes by this method was successfully conducted and investigated by Zuber /5,6/. The third experiment on photochemical separation was carried out successfully by Kuhn et al. /7/. They excited selectively ClO_2 molecules by the radiation of a mercury lamp at the lines 3663 Å and 3654 Å. During the second world war the possibility of photochemical separation of uranium isotopes /8/ was studied, but the optic method could not compete with the industrial gas-diffusion separation method.

After the war in some countries they continued to elaborate the photochemical method of mercury isotope separation /9-16/ and created laboratory units to separate small amounts of various mercury isotopes /15,16/ . Luiti et al. carried out successfully the photochemical separation of carbon and oxygen isotopes /17,18/ with CO molecules excited selectively by an intensive iodine line. In all the successful experiments /3-18/ they employed coincidences of strong lines of atomic spontaneous emission with atomic and molecular absorption lines. Since the number of such coincidences was very limited and the intensity of narrow lines of spontaneous radiation was low, the photochemical separation method with ordinary radiation sources employed was not widely practical despite its obvious potential advantage, noted as far back as in the first works, of a high degree of enrichment in the single separation process.

The creation of laser had permitted above all to revert to the idea of photochemical isotope separation with a more convenient source of monochromatic radiation employed. The first experiment in this direction was carried out in 1966 by Schawlow et al. /19-20/ who accomplished a selective excitation of bromine monoisotopic molecules by the radiation of ruby laser and a photocatalysis of olefine bromination reaction. Although they could not separate the ^{79}Br and ^{81}Br isotopes because of non-selectivity of the photochemical reaction, their work displayed promise for laser in selective excitation of atoms and molecules with particular isotopes at the proper monochromatism and radiation frequency control.

The most important thing is that lasers have allowed to extend largely the sphere of optical isotope separation owing to new methods in selective action of laser radiation on a substance, that was impracticable with pre-laser sources of monochromatic radiation. These new possibilities are based on the following properties of stimulated emission:

1) Stimulated emission can be obtained at any frequency in the IR, visible and UV regions of spectrum;

2) Stimulated emission may exhibit a high intensity quite sufficient to saturate the absorbing transition that is to excite a major portion of absorbing atoms or molecules;

3) Stimulated emission may be far shorter than the lifetime of atomic and molecular excited states;

4) Stimulated laser radiation has high spatial coherence that makes it possible to collimate the beam to obtain a long optical path in the cells;

5) Stimulated radiation has high temporal coherence that makes it possible to elaborate special methods impracticable with incoherent radiation.

The advent of intens IR lasers open the way for isotope separation through selective excitation of vibrational levels of particular isotopic molecules, that is by the method of vibrational photochemistry /21/.

High intensity of laser radiation in the visible, UV and IR ranges has made it possible to develop very general photophysical methods of selective action on atoms and molecules: two-step selective ionization of atoms /22,23/, two-step selective photodissociation of molecules /23-26/, selective multiphoton dissociation of molecules /27,28/.

The advanta [illegible] otophysical processes based on ionization or dissociation, compared to the usual photochemical process, can be understood from simple qualitative considerations if we compare the photochemical reaction of selectively excited molecules with the process of two-step photodissociation (Fig.1). In a single step photochemical process a selectively excited atom or molecule takes part in the three competing processes: 1) a wanted chemical reaction with an acceptor with its rate K; 2) the transfer of excitation to a particle with an unwanted isotopic composition with its rate Q; 3) excitation relaxation and return to the ground state. The high selectivity of a photochemical process is conditioned by:

$$K \gg Q \qquad (1.1a)$$

while the high efficiency by:

$$K \gg 1/\tau \qquad (1.1b)$$

Since all these three processes can take place with one and the same type of collision and the relation between their rates does not depend on the intensity of laser radiation the type of photochemical reaction, the level to be excited and experimental conditions should be chosen properly to meet conditions (1.1). In other words, single-step photochemical processes are inadequately controlled by laser radiation.

In a two-step process the selectively excited atom or molecule is acted upon by the second intensive laser radiation, the object of which is to ionize an atom (molecule) or to dissociate a molecule with the W rate exceeding the rates Q and $1/\tau$ for transfer and relaxation of excitation respectively. Since the probability of photoionization or photodissociation is proportional to radiation intensity I the conditions for high selectivity and high efficiency

$$W(I) \gg \frac{1}{\tau_1} Q \qquad (1.2)$$

can always be met. These considerations hold true for other photophysical processes of ionization and dissociation, in particular for multistep atomic photoionization and multiphoton molecular dissociation. In all these cases, of course, certain requirements on selectivity of secondary processes with the participation of ionization and dissociation products should be fulfilled. Considerable advantages and flexibility of photophysical processes of isotope separation have been demonstrated in experiments on nitrogen isotope separation by the method of two-step photodissociation of ammonia /26/, and on boron and sulphur isotope separation by multiphoton dissociation of BCl_3 and SF_6 molecules /27,28/. Isotope separation by the method of two-step molecular photoionization has been studied in works /23,29/, though not realized practically yet.

In this classification of single-step photochemical and two- (or more) step or multiphoton photophysical processes there is an important exception, that is processes with internal rearrangement of atoms and molecules after selective excitation which need no additional external action. For example, when certain quantum atomic states are resonantly excited, the excited electron shell may be reconstructed, with the result that the atom becomes ionised. Such a process is called autoionization or preionization. In much the same way, when certain molecular electronic states are subjected to a resonant selective excitation an internal rearrangement of electrons comes about, as a result of which the molecule may dissociate or an atomic rearrangement occurs that is molecular isomerization. If the processes of internal reconstruction in atoms or molecules have the sufficiently high rate S, that is

$$S >> \frac{1}{\tau_1} Q \qquad (1.3)$$

then a high selectivity and efficiency can be attained in the single-step process. Isotope separation through selective molecular photopredissociation has been considered in /30,31/, and in work /30/ separation of H and D isotopes through photopredissociation of formaldehyde molecules was demonstrated.

A photophysical approach, based on change of atomic or molecular trajectory during photon absorption owing to momentum transfer, can be also applied to laser isotope separation. This method of isotope separation under the action of laser resonance emission was suggested in works /32,33/ and recently experimentally conducted in work /34/. This method employs a high spatial coherence (directivity) of laser radiation. One can conceive other methods of laser isotope separation based on the change in polarizability, angular momentun and on other characteristics of atoms and molecules when excited. Probably, various versions of separation methods are practicable when they apply the characteristic features of coherent interaction between laser radiation and atoms and molecules, and, in particular, the effect of adiabatic particle excitation in a light field with a scanning frequency, the effect of coherent oscillations of a particle between levels, etc.

So, there are many ways for isotope separation by acting selectively on atoms and molecules of a particular isotopic composition. All these ways are considered in the review. Yet, at first it would be better to classify all possible methods of laser isotope separation. Fig. 2 illustrates conditionally possible ways to use the selective excitation of atoms for isotope separation. Apart from the methods already mentioned, to make the picture complete, fig. 2 displays also those employing the autoionization of excited atoms under the action of the external electric field and the ionization of excited atoms as they come in collision with acceptors capable to capture an electron. In much the same way fig.3 shows possible ways to use the selective excitation of molecules for isotope separation.

All the methods shown in Fig.2 and 3 are outlined in this review. The review is divided into two parts. Part I includes § 2-5 in addition to the Introduction, and Part II - § 6-11. In § 2 consideration is given to the problem of selective excitation of atoms and molecules with a particular isotope, the problem being common for all the methods. Isotope shifts in substance spectra in various agregate states, methods of spectral line narrowing and the possibility to use narrow nonlinear resonances to raise the excitation selectivity are studied here. In § 3 methods of selective ionization for atoms and molecules are set forth. It describes the well -known experiments on selective ionization of Rb, and U atoms, the conditions of optimum use of laser radiation in small and large volumes, methods of increasing the ionization probability of excited atoms by means of autoionization, field-induced ionization. Methods of ionization of excited atoms, when they come in collision with electron acceptors and with other excited atoms, are briefly discussed. In § 4 consideration is given to isotope separation by the method of two-step molecular photodissociation. At first, the dissociation through an intermediate vibrational state is discussed, and the photodissociation band shift with molecular vibrations excited in particular. The effects decreasing the dissociation selectivity are considered: distribution of molecules on rotational states, thermal excitation of molecules, large width of dissociation band. Comments on the optimum use of exciting and dissociating radiation in small and large volumes are made. Here some experiments on selective two-step photodissociation of HCl and NH_3 molecules are described. In § 5 methods of selective molecular photopredissociation and photoisomerization are set forth, experiments on photopredissociation of the H_2CO, ortho-I_2 and Br_2 molecules in the main. Predissociation of excited molecules during collisions and in an external magnetic field is discussed. And in conclusion the method of isotope separation based on molecular photoisomerization is described and the molecules possible for this method are given.

Part II, to be published in the next issue, describes in the beginning (§ 6) the method of selective molecular dissociation by a strong IR laser field. The method elaborated quite recently /27,28/ is not so apparent, as opposed to all other methods, but more simple and efficient. Here an experiment on isotopically-selective dissociation of BCl_3, SF_6 and OsO_4 molecules is being described. The review presents the data on kinetics of enrichment of residual (undissociated) gas and molecules created by chemical binding of dissociation products. The effect of isotopically-selective dissociation when acting on weak overtone and compound molecular vibrations is under discussion. § 7 is devoted to the oldest and well-known method of optical isotope separation, that is the method of photochemical reactions of electron-excited atoms and molecules. In its beginning experiments conducted with conventional light sources are reviewed, and their conceptual and instrumental limitations are analyzed. Experiments on selective chemical reactions of ortho-I_2 molecules (separation of ortho- and para-I_2) and ICl, Cl_2CS molecules (separation of chlorine isotopes) are described. In § 8 consideration is given to the most difficult method of photochemical separation during vibrational excitation of molecules by IR laser radiation. First the general questions on reactivity of vibration-excited molecules, influence of a certain vibrational excitation on the chemical reaction rate, relaxation of vibrational excitation are studied. Then, on HCl molecules, the method is considered which employs chemical reactions of molecules excited directly by laser radiation to low vibrational levels (v =1,2), that is, reactions with $E_a \simeq \hbar\omega$. The basic difficulties, such as molecular reactions due to thermal excitation and heating at laser excitation, are analyzed. The conditions at which selective reactions are practicable are formulated. Then the method is considered which employs excitation of high vibrational states due to vibrational-vibrational exchenge, that is, chemical reactions with $E_a >> \hbar\omega$. In § 9 separation schemes are described in which the change of atomic trajectory during resonant interaction with the light field is applied and, in particular, an experiment with a beam of Ba atoms.

§ 10 is devoted to economic and technical aspects of laser isotope separation. The efficiency of the laser separation method is compared with that of other methods. The cost of different methods of uranium isotope separation is discussed separately as well as the advantages of the laser method in this case. In conclusion consideration is given to use of isotopic materials in large quantities at a low cost of separation. § 11 deals with some problems related directly to laser separation. High-rate separation of nuclear isomers and its application to preparation of an active medium for γ - lasers is discussed here as well as the problem on laser methods of production of highly pure substances and on the new laser technology in this area. At last detection of single atoms and molecules is considered separately, a problem which will be solved automatically in elaborating effective methods of laser isotope separation.

2. Spectral Shifts and Selective Excitation.

The first step of any laser isotope separation scheme /35,36/ is absorption of a laser photon by the desired isotopic atom or molecule at a wavelength for which the undesired isotopic species is relatively transparent. Thus, a transition with an isotopic shift greater than its linewidth is needed. The spectrum should not be so dense that the shift only results in a coincidence with another absorption feature of the unwanted isotopic species. The laser should have a spectral resolution and tunability sufficient to excite the desired transition within its linewidth. Following the excitation it is then essential that the separation step occur before nearly-resonant energy transfer to the undesired isotopic species takes place. In this section we discuss the sources and magnitudes of isotopic shifts in atomic and molecular spectra. Linewidths of transitions are compared to isotopic shifts and to spacings characteristic of the spectral structure of various types of transitions. The influences of temperature, pressure and physical state on these comparisons are noted. Non-linear optical line-narrowing techniques such as two-photon and saturation resonance spectroscopy are considered. Finally, some of the practical problems of selective excitation are illustrated using formaldehyde as an example.

The electronic energy levels of atoms are shifted by changes in the number of neutrons in the nucleus through the change in total nuclear mass, the change in nuclear volume and therefore charge distribution and the change in nuclear spin angular momentum/37-39/. The effect of nuclear mass on the reduced mass for electronic motion about the nucleus gives an isotope shift of order of magnitude

$$\Delta\nu \sim \nu \frac{m\ \Delta M}{M^2} \tag{2.1}$$

where m is the electron mass, M the nuclear mass and ΔM the isotopic mass difference. It is important only for light elements. Shifts of about 1 cm^{-1} are observed for ^{6}Li, ^{7}Li. For heavier elements the shifts are dominated by the change in hyperfine structure, interaction of nuclear and electronic angular momentum, and the change in nuclear volume. The change in nuclear volume shifts the energies of s electrons and therefore, gives substantial isotope shifts for transitions involving s electrons. The volume shift is dramatically illustrated by the uranium II transition shown in Fig. 4(a). Fig. 4(b) shows the combined effect of volume shifts and hyperfine structure. Hyperfine structure multiplets occur for ^{199}Hg and ^{201}Hg and single lines for masses 198, 200, 202 and 204.

In molecular spectra the structure of vibrational and rotational energy changes is superimposed on the electronic energy changes. In addition to these rovibronic transitions we will be interested in transitions where only vibrational and rotational energies change. In molecular spectra the isotopic shifts are dominated by the effect of nuclear mass on the vibrational energy spacings (inversely proportional to the square root of the vibrational reduced mass) and the rotational energy level spacings (inversely proportional to the moments of inertia). The spectra of linear molecules are generally quite simple; each vibrational or vibronic band consists of a regularly spaced set of individual rotational transitions. The space between lines is much greater than the linewidth for molecules containing the lighter elements and only begins to approach the linewidth for molecules with moments of inertia as large as I_2 /40/. The rotational structure in the bands of non-linear molecules---asymmetric tops, spherical tops and to a lesser extent symmetric tops---is far more complex. Fortunately, for many simple molecules, gas phase electronic and vibrational spectra are still sufficiently well-resolved that the spectra of different isotopic molecules are clearly resolvable. But for many molecules the rotational structure is so closely spaced that lines overlap within their Doppler widths. Such a situation is demonstrated by the laser spectroscopy of the 10μ transition of SF_6 /41/ and OsO_4 /42/. However the presence of a great number of absorption lines, though, does not exclude the possibility of accidental occurrence of a section in the absorption spectrum on which the absorption line of just one isotopic molecule falls. For illustration, Fig.5 presents the vibrational-rotational spectrum of absorption of monoisotopic OsO_4 molecules obtained by the method of absorption saturation with the help of some lines of CO_2 laser /42/. The typical interval between absorption lines is much smaller than Doppler width, but the line R (8) of CO_2 laser at 10.6 mcm, for example, is absorbed mainly by $^{189}OsO_4$ molecules. For heavy molecules the problem with closely spaced rotational lines is compounded by the overlapping absorption spectra of molecules populating the low lying vibrational states. The electronic excited states of many simple molecules are often strongly perturbed and extremely complex. For example, only a few lines in the entire visible spectrum of NO_2 have been resolved and analyzed.

Gas phase absorption lines are broadened by the Doppler effect, by molecular collisions, by radiative decay, by radiationless processes, by passing through the region of interaction with the optical field and by power broadening. At low pressures the Doppler effect usually dominates the linewidth. The width is given by

$$\Delta\nu_D = 7.2\text{x}10^{-7}\ \nu\ (T/M)^{1/2} \tag{2.2}$$

where T is the temperature in °K and M is the molecular mass in atomic mass units. Clearly the Doppler width may be reduced by lowering the gas temperature. Low temperatures may be achieved at gas densities above the equilibrium vapor pressure by supersonic expansion through nozzles such as have been used for spectroscopy/43,44/, for molecular beam sources /45/ and for gas dynamic lasers /46-48/. In systems where low vapor densities are feasible the Doppler width may be nearly eliminated by carrying out the excitation perpendicular to a well-collimated molecular beam /49/.

Spectral line narrowing in atomic (or molecular) beams makes it possible to realize isotopically - selective excitation of particles even when the isotope shift is smaller than the Doppler width of a transition for particles in equilibrium gases. Such experiments have been conducted on beams of Ba /34/ and Ca /50/ atoms. The disadvantage of low operating densities is that large absorption cross sections and long optical paths are required for efficient use of the laser energy. An upper limit on the operating pressure in bulk gases is often imposed by pressure broadening. Fig. 6 shows the line shapes for formaldehyde at several pressures. Notice that if particularly high selectivity ratios are required that the tails of the lines become important. They are dominated by pressure broadening and by lifetime broadening since the

Lorentz profile decreases quadratically rather than exponentially with displacement from line center /51/.

The absorption spectra of molecules trapped in matrices of rare gases or other inert molecules at low temperature are often quite sharp /52/. Molecular rotation is usually stopped and the spectra exhibit only changes in electronic and vibrational energy. Spectral linewidths of less than 1 cm^{-1} can often but by no means always be obtained. Isotope shifts for Cl and lighter elements are normally well resolved. An observable shift has even been reported for a uranium compound, Fig. 7 /53/. Matrix spectra are often complicated by the presence of more than one type of trapping site and by the presence of dimeric and polymeric units of the isolated molecule.

The spectra of liquids are so broad that spectral shifts are likely to be resolvable only for the first few elements.

Non-linear spectroscopic methods allow isotopic selectivity to be achieved for isotope shifts which are smaller than the Doppler linewidth but larger than the Lorentz (homogeneous) width. The Lamb-dip may be exploited by tuning the laser to the exact line center of the undesired isotope /23,54,55/. In a standing wave field (two oppositely directed beams), when the laser frequency ν is coincident with the absorption line center of the unwanted isotope and saturation is strong enough, the efficiency of excitation is reduced by 40% compared to the efficiency of excitation of molecules whose absorption line center is out of resonance with laser frequency ν. A much more selective excitation may be carried out using the simultaneous absorption of two photons from oppositely directed beams of nearly or exactly the same frequency /56,57/. Vasilenko, Chebotaev and Shishaev /58/ pointed out that for two-photon absorption in a standing wave the Doppler shift of an absorber for one running wave component is exactly equal and opposite to that for the oppositely directed wave. Thus within a Lorentz width of the line center all molecules are in two-photon resonance for one photon from each of the running waves. Only those molecules with near-zero velocity are in resonance for two photons from a single running wave. Off line center, only molecules whose velocity Doppler shifts them into resonance with two photons of a single running wave will absorb. The ratio of line center absorption to the Doppler profile wings is approximately half the ratio of the Doppler to the Lorentz width. If two oppositely directed beams differing in frequency by more than the Doppler width are used, still higher selectivity is possible. This effect was demonstrated in high resolution spectroscopy by several groups in 1974 /59-61/. The application of this technique to selective excitation and isotope separation has been discussed in /56,57,62/. Very high laser powers are required for efficient absorption of the laser light. These powers may be considerably reduced if a nearly resonant intermediate state enhances the two-photon cross section. This effect was demonstrated experimentally on atomic transition in /63/. The estimations done in /56,64/ show that this effect may be of importance for vibrational-rotational molecules as well. The first successful experiments on two-photon molecular absorption with Doppler width reduction have been carried out in work /65/ on CH_3F molecules. The situation for atoms is much more favorable than for molecules because molecular transition strengths are spread out over the entire vibration-rotation structure. If the two-photon resonance is to be used to excite states for which the rotational structure is overlapped within a Doppler width, the laser frequency must be completely outside the rotational envelope of any intermediate energy states. Otherwise, non-selective sequential absorption of two photons through a real intermediate state will occur. This places a severe limitation on resonant enhancement for many systems of practical interest.

As the number of neutrons varies, the nuclear spin variation may change substantially selection rules. As a result, atoms of some isotopes may acquire lines which are forbidden for other isotopes. This effect of induction of electric dipole transitions due to electron-nucleus interaction is essential for transitions $J = 0 \rightarrow J' = 0$ forbidden for all multipoles. On account of nuclear spin an atom has the total angular momentum $F \neq 0$ which alters the selection rules. The forbidden lines 2270 Å ($6^3P_2-6^1S_0$) and 2656 Å ($6^3P_0 - 6^1S_0$) found by Rayleigh in 1927 and Wood in 1928 respectively in the odd isotopes ^{199}Hg ($I=1/2$) and ^{201}Hg ($I = 3/2$) are a classical example of this effect. Ya.B.Zeldovich and I.I.Sobelman have pointed recently /66/ to the possibility of using this effect in selective excitation and laser separation of even or odd isotopes of the following elements (Hg, Sr, Ba, Zn, Cd). A large spectral line shift, which is much higher than the isotope shift, is typical of such selective excitation with respect to nuclear spin.

Due to change in the nuclear spin parity new lines appear in the spectra of diatomic homonuclear molecules. For example, ortho-para molecular modifications have additional sets of electron-vibrational-rotational lines that allow selective excitation of isotopes with even and odd total nuclear spins of molecules. In the infrared vibrational-rotational spectrum, as one of the atoms is substituted by another isotope, the forbiddenness of electric dipole transitions is eliminated. Most vividly this effect shows up in the IR spectrum of HD, HT and DT molecules.

A relatively large amount of effort has been devoted to the selective excitation and photochemistry of the first excited singlet state of formaldehyde, H_2CO /67/. Figure 8 shows a small portion of the spectrum of H_2CO and of $H_2{}^{13}CO$ /68/. The instrumental resolution of 0.1 cm^{-1} is broader than the 0.06 cm^{-1} Doppler width (FWHM). The selectivity of excitation of the $H_2{}^{13}CO$ spectrum has been demonstrated /69/ by scanning a frequency-doubled, N_2-pumped dye laser (Molectron Corp.) with a bandwidth of 0.1 cm^{-1} through the spectrum in Fig. 8. The fluorescence from a cell containing natural formaldehyde, $H_2{}^{12}CO$: $H_2{}^{13}CO=89$, and another containing an enriched sample, $H_2{}^{12}CO:H_2{}^{13}CO= 0.10$, was observed. Near 28250 cm^{-1} a fluorescence intensity 90 times greater for the $^{13}CH_2O$ was observed. The selectivity is thus at least 10^2 and possibly larger. The absorption cross section at this wavelength is about 10^{-20} cm^2. For efficient isotope separation a laser at this wavelength with a resolution and long term stability of better than 1 GHz is required. For 63% absorption of the laser energy the product of path length and pressure of the desired isotopic species must be 30 meter·torr. In order to remove 63% of the desired isotope from the sample 60 Joules/cm^2 must pass through the sample.

For comparison let us give the same estimation for the two-photon excitation method. For two-photon excitation the cross section is roughly 2×10^{-34} cm^4/watt for a Doppler linewidth /70/. There are no resonant intermediate states. A pressure broadening coefficient of 7×10^{-4} cm^{-1}/torr from ground state microwave data /71/ gives a pressure independent absorption coefficient/62/ at the resonance peak of $b = 6 \times 10^{-16}$ cm^{-1}(cm^{2}W^{-1}) for pressures such that the collision rate is greater than the predissociation rate, $P \geq 1$ torr. This absorption coefficient must be multiplied by the fractional abundance of the desired isotope. For efficient photon absorption laser power must be on the order of $1/b\tilde{\nu}$ or 5×10^{12} W for $^{13}CH_2O$ /62/. The laser intensity must be kept low enough so that power and optical Stark broadening do not increase the linewidth. This requires $I < 10^{12}$W/cm^2 /62/. For $I = 10^{10}$ W/cm^2 a cell of 500 cm^2 cross section and 1.5×10^5 m is needed. For practical conditions for two-photon excitation method with H_2CO a very low efficiency would be achieved.

Selective excitation of molecules in a gas phase is usually conducted by lasers with the spectrum width being much smaller than the isotope shift and absorption linewidth. Single-frequency lasers with a narrow radiation line are required to excite selectively those molecules having a broad electron-vibrational-rotational spectrum with overlapping absorption regions of two isotopic molecules. This sharply reduces the number of simultaneously excited molecules owing to their distribution over rotational sublevels. For isotopically selective excitation one can use broadband radiation without the spectral components corresponding to the absorption lines of those isotopic molecules the excitation of which is undesirable /72/. The radiation of lasers with a broad generation spectrum and with an absorber in the cavity has a suitable spectral composition/73/. If such a laser irradiates a molecular mixture, the molecules not in the cavity will be excited for the most part. This possibility of selective molecular excitation by a broadband spectrum has been experimentally demonstrated in work /72/ with the use of $H_2C_2O_2$ molecules and a pulsed dye laser.

3. SELECTIVE MULTISTEP PHOTOIONIZATION

Selective atomic photoionization can be conducted by some schemes the common feature of which is a previous selective excitation of one or several intermediate excited levels with laser radiation and a subsequent ionization of only excited atoms with an additional laser radiation or when they collide with other particles. Fig.9 illustrates some possible schemes of selective atomic ionization of special interest for laser isotope separation. The two-step photoionization scheme is the simplest of them /22/. The three-step scheme may be of use, say, for atoms with a high ionization potential /74/. The photoionization cross-section can be increased by tuning the frequency of secondary radiation to that of the transition to an autoionization (spontaneous /75/ or electric-field-induced /76/) state. Finally, excited atoms can be ionized when collided with other particles (electron acceptors /77/ or excited atoms /78/).

First let's consider in more detail the two-step atomic photoionization (Fig.9a). In the two-step photoionization scheme the radiation of the first laser transfers atoms from the ground state "1" to an excited state "2". At the same time the atoms are exposed to the pulse of the second laser the quantum energy $\hbar\omega_2$ of which is inadequate to photoionize the atoms from the ground state but sufficient to photoionize them from an excited level:

$$\hbar\omega_1 + \hbar\omega_2 > E_i \, , \quad \hbar\omega_2 < E_i \qquad (3.1)$$

The rate of atomic excitation under the action of a continuous radiation is determined by the expression:

$$W_e = \frac{\sigma_e P_e}{\hbar\omega_1} ; \quad \sigma_e = \frac{\lambda_1^2}{2\pi} \frac{A_{12}}{\Delta\omega} , \tag{3.2}$$

where σ_e is the cross-section of the radiation transition 1-2, A_{12} is the Einstein coefficient of transition, $\Delta\omega$ is the line bandwidth of transition, P_e is the power of exciting radiation (W/cm^2) falling within the spectral range of absorption line. If the relaxation time of an excited level equals to τ the population of the intermediate state under excitation will be:

$$N_2 = N_1 \frac{g_2}{g_1} \left(1 + W_e \tau\right)^{-1} \tag{3.3}$$

To saturate the transition 1-2 the power of exciting radiation should comply with the condition:

$$P_e \gtrsim \mathcal{P}_e = \frac{\hbar\omega_1}{2\sigma_e \tau} , \tag{3.4}$$

where $\mathcal{P}_e$ is the power of exciting transition saturation. When the relaxation time of excited level population is determined only by radiation decay to the ground state, that is $\tau = A_{21}^{-1}$, the saturation power doesn't depend on level lifetime:

$$\mathcal{P}_e = \pi \frac{g_1}{g_2} \frac{\hbar\omega_1}{\lambda_1^2} \Delta\omega \tag{3.5}$$

The photoionization rate of an excited atom under a continuous radiation with its power P_i is given by the expression:

$$W_i = \frac{\sigma_i P_i}{\hbar\omega_2} , \tag{3.6}$$

where σ_i is the photoionization cross- section. For each excited atom to be ionized with a probability of about unity the power of ionizing radiation should comply with the condition analogous to (3.4):

$$P_i \gtrsim \mathcal{P}_i = \frac{\hbar\omega_2}{\sigma_i \tau} = \frac{\hbar\omega_2}{\hbar\omega_1}\,\frac{\sigma_e}{\sigma_i}\,2\mathcal{P}_e \qquad (3.7)$$

To ionize all excited atoms the radiation power required should exceed the power of exciting radiation approximately in the ratio ($2\sigma_e/\sigma_i$).

As an example let's consider the two-step photoionization of Rb-atoms through the first intermediate level $5p\ ^2P_{1/2}$ (Fig.10a). For Rb-vapor at 100°C (the Doppler width $\Delta\omega = 4.10^9$ sec^{-1}) the radiation transition cross-section $\sigma_e = 10^{-11}$cm^2, the cross-section of excited level photoionization $\sigma_i \simeq 10^{-18}$cm^2. The saturation power of the absorption line $\lambda_1 = 7950$ Å $\mathcal{P}_e = 0.5$ W/cm^2, and the power, required to photoionize atoms with the same probability as that of excitation, $\mathcal{P}_i = 1.6.10^7$ W/cm^2(the radiation decay time of the $^2P_{1/2}$ level $\tau = 2.6.10^{-8}$sec, $\lambda_2 = \lambda_2^B = 4730$ Å). Thus, to excite each atom and ionize each excited atom substantially different powers are wanted. This is quite natural since the first process is resonant and the second one is non-resonant.

The requirement for power level of ionizing radiation falls off markedly if the intermediate level is metastable. The saturation power of resonance transition, provided the relaxation mechanism is radiation, doesn't depend on the lifetime of the upper level and the $\mathcal{P}_i$ power drops proportonally with increase in the lifetime of the intermediate level. This is true as long as the level lifetime is shorter than the time of interaction between atom and light beam. An atom moving with the v_0 velocity interacts with a light beam of a limited diameter a during the time $\tau_{int} = a/v_0$. For example, if a hot heavy atom moves with $v_0 = 3.10^5 \frac{cm}{sec}$ and the beam diameter a = 1 cm the interaction time $\tau_{int} = 3.3\,10^{-6}$ sec. Therefore it is advisable to use intermediate states with $A_{21} \simeq 1/\tau_{int} = 3.10^5 sec^{-1}$ that will reduce the P_i power to a value in the order of 10^5 W/cm^2.

It is practicable to bring about two-step photoionization under the action of short radiation pulses with their duration τ_1, τ_2 shorter than the relaxation time τ of intermediate level population; they are time-synchronized with the accuracy $\Delta\tau$ shorter also than τ. To excite a considerable part of atoms and then to photoionize the most portion of excited atoms under such conditions the density of pulse energies should comply with conditions analogous to (3.4) and (3.7):

$$E_e \gtrsim \mathcal{E}_e = \frac{\hbar\omega_1}{2\sigma_e} \quad , \qquad (3.8)$$

$$E_i \gtrsim \mathcal{E}_i = \frac{\hbar\omega_1}{\sigma_i} \qquad (3.9)$$

For the case of two-step ionization of Rb-atoms considered above energies of exciting and ionizing radiations should exceed the values $\mathcal{E}_{exc} = 1.2.10^{-8}$ J/cm^2 and $\mathcal{E}_i$ =0.42 J/cm^2 and durations must be shorter than the time τ = 26 nsec.

The first experiment on selective two-step atomic photoionization was conducted in work /22/. Fig.10 illustrates schematically the levels of Rb-atom used in photoionization and gives the experimental scheme. The radiation of the tunable dye laser at $\lambda_1 = 7950$ Å transferred a portion of Rb-atoms to the state $5p\ ^2P_{1/2}$. Excited atoms were photoionized by a radiation pulse of second harmonic of the ruby laser used for dye solution pumping. The second-harmonic quantum energy was sufficient to photoionize excited Rb-atoms ($E_i - \hbar\omega_1 = 2.62$ eV) but not sufficient to photoionize the atoms from the ground state ($E_i = 4.18$ eV). Both the laser pulses were directed to a gas cell with Rb-vapours at 10^{-3} torr. As the wavelength of the tuned laser was tuned to the absorption line of Rb, a sharp increase of photocurrent signal could be observed. In experiment /22/ photoionization was done in a gas cell with no ion extraction.

Selective ionization of Rb atoms has been studied in more detail in work /79/ where conditions (3.8) and (3.9), under which every atom being in resonance with exciting radiation is ionized throughout one pulse, are realized. The authors of this work have investigated ion extraction through electric field ($\sim 10^{13}$ ions/cm^3 in one pulse) and the dependence of photoionization cross-section on the excess of the energy of the second photon over the ionization limit.

Another important experiment was carried out in work /80/ with a beam of uranium atoms. The experiment is schematically shown in Fig.11. A collimated beam of ^{235}U and ^{238}U atoms mixed was irradiated by a dye tuned laser the c.w. radiation of which at $\lambda_1 = 5915.4$ Å excited the atoms of U -isotope only. At the same time the atoms of the beam were illuminated by UV-radiation of a mercury lamp over the spectral range 2100 Å-3100 Å. The short-wave boundary of this range is conditioned by the absence of photoionization of non-excited atoms, while the long-wave one is determined by the threshold energy of photoionization of excited atoms. The ions of ^{235}U$^+$ formed were separated from the beam of neutral atoms by the electric field and entered a quadrupole mass spectrometer. Experiments were conducted with natural (0.7%) content of ^{235}U in the mixture as well as with a mixture enriched in ^{235}U-isotope. Fig.12 shows the results of experiments on selective photoionization of various uranium isotopes in the natural mixture. When the laser frequency was tuned to the absorption line of a particular uranium isotope the mass spectrometer had the line of just this isotope. The photocurrent signal in selective photoionization of ^{238}U was 10^3 times more than that in photoionization of ^{235}U. This derives from the fact that, firstly, the content of ^{235}U-isotope in natural mixture is 140 times less than that of ^{238}U-isotope and, secondly, the absorption line of

^{235}U, in contrast to the line of ^{238}U, is split into 3 components of hyperfine structure and the laser radiation can be tuned not only to one component.

Experiments on selective atomic photoionization with the object of working out methods of isotope separation are being conducted now by some laboratories in several countries. By way of example, at the VIII International Quantum Electronics Conference along with experiments on uranium the results of studies on Ca-isotope separation were presented by scientists from West Germany . Excitation was done from the metastable level $4p\ ^3P_2$ to the level $5s\ ^3S_1$ ($\lambda_1 = 6182\ \overset{o}{A}$) by radiation of c.w. dye laser, while excited atoms were ionized by radiation of argon laser at $\lambda_2 = 4888\ \overset{o}{A}$. The quantum efficiency of two-step ionization for one metastable atom ranged between 10^{-3} and 10^{-2}.

Experiments /80/ on selective ionization of uranium atoms can be considered as the first step in developing a new method of U-isotope separation on a commercial scale. Formally /81/ R.L. Dickeman, the president of "Exxon Nuclear Co." USA had reported on successful experiments on U-isotope separation under laboratory conditions. This firm took out a patent /75/ for process of U-isotope separation through the method of selective two-step photo-ionization and placed the work on a broad footing in this direction /82/.

Some results of this work obtained, as the authors say, in the early stage of investigation of the method in 1971 have been recently reported at the II International Conference on Laser Spectroscopy /83/. At the same time the Livermore Laboratory USA presented the results of its latest experiments on two-step ionization of uranium atoms (excitation with the 3781 Å line of a xenon ion laser, ionization with the 3500 Å line of a krypton ion laser). The ion yield rate of $^{235}U^+$ in their experiments was $2 \cdot 10^{-3}$ gr/hr, that is 10^7 times higher than the rate obtained in the early experiments /80/.

To accomplish a highly-efficient process of isotope separation by the selective ionization method on a practical scale the conditions as follows should be met:

1) All atoms in an unexcited beam should be in the ground state, and ions must not exist. If atoms of a selected isotope are distributed over several levels or sublevels a multifrequency radiation, exciting atoms from every sublevel, is needed to remove completely the selected isotope from the isotope mixture. The thermal ions existing in the atomic vapour must be removed.

2) The laser radiation should perform selective photoionization for each atom of a selected isotope. Powers needed for this purpose are given by relations (3.4) and (3.7).

3) The laser radiation intensity should be used practically in full to excite and ionize atoms of a selected isotope.

4) There shouldn't be transfer of excitation or charge between isotopes under separation.

Let's consider now the possibility of fulfilling conditions (3) and (4). To do this one must keep in mind the most interesting elongated geometry of installation for isotope separation. In this case the atomic beam is emitted by a long "sheet" source along which a laser radiation travels, as is shown in Fig.13.

The coefficient of linear absorption per unit length for exciting radiation $\varkappa_{exc}=N_{10}\sigma_{exc}$; where N_{10} is the density of atoms in the ground state, and the absorption coefficient of ionizing radiation $\varkappa_i=N_2\sigma_i$ .Thus, the penetration of exciting radiation with a weak absorption saturation $\ell_{exc}^{0}=(N_{10}\sigma_{exc})^{-1}$, and with a strong saturation of transition, that is when $P_{exc}\gg\mathcal{P}_{exc}$, the penetration rises accordingly to the value $\ell_{exc}\simeq\ell_{exc}^{0}\frac{P_{exc}}{\mathcal{P}_{exc}}$. As absorption is saturated at the transition 1-2 the intermediate level population $N_2\simeq\frac{1}{2}N_{10}$ and, hence, the penetration of ionizing radiation will be:

$$\ell_i\simeq\frac{2}{N_{10}\sigma_i}=\ell_{exc}^{0}\,2\frac{\sigma_{exc}}{\sigma_i} \qquad (3.10)$$

The penetration of ionizing radiation is deeper by the factor $2\frac{\sigma_{exc}}{\sigma_i}$ than that of exciting radiation. According to (3.7) the same factor appears in the ratios between the powers needed to excite and ionize each atom. Physically this is quite clear. Because of the difference in cross-section of resonance excitation and photoionization of atoms materially different powers $\mathcal{P}_{exc}$ and $\mathcal{P}_{i}$ are required to excite and photoionize them. But for each atom to be excited and ionized, energies of the same order $\hbar\omega_1$ and $\hbar\omega_2$ are consumed. Because of this the exciting radiation will be absorbed at a path which σ_{exc}/σ_i times shorter than that for the ionizing radiation.

To use the exciting radiation in full the path length should be $L \simeq \ell_i$. For example, for the case of two-step photoionization of Rb-atoms in a beam with the atomic density $N_{10}=10^{13}cm^{-3}$ the value ℓ_i = 200 m and ℓ_{exc}^{o} = 10^{-2}cm. Thus, it is impracticable to ensure the similar absorption of exciting and ionizing radiations as they travel along the sheet atomic beam. It is possible to use a transverse propagation of the exciting beam and a longitudinal one of the ionizing beam (Fig.13), but this presents a severe problem in introducing the optical radiation into the vacuum chamber of the unit. Therefore a considerable part of publications on selective atomic ionization is aimed at search for methods which will allow an increase in the cross-section of excited atom ionization. The main ones are listed below.

In work /75/ a special attention is paid to the possibility of increasing photoionization cross-sections with autoionization resonances used. By autoionization is meant a process of spontaneous transition of an atom from a discrete excited state to an ionization state. Autoionization may occur when continuous and discrete energy levels exist simultaneously above the ionization limit, that is practicable either in a simultaneous excitation of two valence electrons or in excitation of electrons from the inner atomic shell. To cite an example, according to the data from work /85/ in the spectrum of photoionization of $Mg\,\bar{I}$ from the excited state $3s3p\ ^1P^o_1$ there are autoionization resonances with $\sigma_i = 5.10^{-16} cm^2$. Such autoionization levels are known to exist in spectra of CuI, AgI, ZnI, CdI, HgI, etc. /86/.

To illustrate the existence of autoionization resonance peaks in continuous absorption, Fig. 14 shows the spectrum of photoionization from the excited state of uranium atom obtained in work /83/ using a tunable dye laser. It is seen that by selecting a wavelength we can control the value of ionization cross-section σ_i.

Work /76/ contains a proposal to use the autoionization of the discrete levels arising below the ionization limit under external electric field. With the use of two or three tuned lasers it is possible to excite in succession an atom to a state with a large value of the principal quantum number n, the excitation efficiency being rather high. The electric field distorts the electronic spectrum of atom so (Fig. 15) that some levels of discrete spectrum closest to the ionization limit fall within the continuum, while other levels become autoionized and the probability of their ionization decay rises with increase in the principal quantum number. It will be the optimum case when an atom is excited by laser radiation to a state the autoionization probability of which is more than the radiation decay probability but less than the Doppler width of transition to a state of autoionization. In this case each excited atom will be ionized, cross-sections of such an ionization being similar to that of the resonant transition between discrete energy levels. The calculations done in work /76/ show that such a method can be accomplished with relatively weak electric fields (below 30 kV/cm) which cause no electric breakdown in the atomic beam. The first successful experiment on ionization cross-section increase by electric field was carried out in work /87/ using Na vapours. Two-step laser excitation converted resonantly the atoms of Na to the highly excited states 12 d - 18 d, and then they were autoionized in an electric field with its intensity of 10 kV/cm. For illustration, Fig.16 shows the dependence of photoelectric current at the varied intensity of the electric field as the wavelength λ_2 of the second laser is tuned within the transition $3^2P_{1/2} - 14^2D_{3/2}$. The state $15^2D_{3/2}$ is 488 cm^{-1} lower than the ionization limit, but the electric field causes autoionization of the atoms. The total cross-section of two-step ionization obtained in the experiment /87/ is about 10^{-14} cm^{-2}, that is 10^{5} times higher than the standard photoionization cross-section for Na.

A certain benefit may be gained in two-step resonance excitation of atoms to a discrete state, spaced not so far from the ionization limit so that an infrared photon suffices to photoionize an excited atom (Fig.9b) /74/. Requirement (3.7) for ionizing radiation power is not so rigid, since at present IR laser radiation is accessible with much higher power when compared to the power of visible radiation.Besides, the efficiency of IR gas lasers (say, CO_2-laser) is much higher than that of a visible laser; because of this, the requirement (3.10) on length of powerful use of ionizing radiation may be relaxed without any increase in consumption of energy.

Some collisional processes, in which excited atoms participate, result in ionization of these latter with a fairly large cross-section. In work /78/ consideration was given to the possibility of ionizing excited atoms A^* of a selected isotope when they collide with excited atoms C^* specially prepared in a gas mixture. In such a process the excited atoms C^*, due to their Van-der-Waals interaction with the excited atoms A^*, induce a high-frequency dipole moment in these latter. The amplitude of this moment may be 3-4 orders in excess of that of polarization, which can be induced directly by laser radiation in the atoms A^* at the transition with atomic ionization. The estimates /78/ show that in this way we can increase the ionization cross-section of the excited atoms A^* by about 3-4 orders.

In report /77/ attention is drawn to the possibility of effective ionization of excited atoms of a selected isotope as they collide with molecules having a high electron affinity. For example, a molecule of SF_6 can trap an electron from an atom lying about 1 eV below the ionization limit with its cross-section $\sigma_i = 2.10^{-15} cm^2$ /88/. In mixtures of excited atoms A^* with molecules, which constitute strong electron acceptors, the process of atomic ionization can be alleviated substantially.

The methods proposed for increasing photoionization cross sections of excited atoms of a particular isotope, basically, up to values of $\sigma_i \simeq \sigma_{exc} \simeq 10^{-12} cm^2$ (with the use of autoionization in the electric field) or at least up to values of $\sigma_i = 10^{-14} cm^2$ will make it possible ,probably, to use practically in full the ionizing radiation in units of reasonable dimensions. For example, if $\sigma_i = 10^{-14} cm^2$ in a beam of atoms with their density $N_0 = 10^{13} cm^{-3}$ and with a selected isotope content of 2% the exciting beam will be absorbed within $\ell_i = 10$ m.

There are two collisional processes which can reduce the ionization selectivity of atoms of a particular isotope and hence the coefficient of laser isotope separation:

1) excitation transfer as excited atoms A^* collide with unexcited atoms B of another isotope;

2) charge transfer between ions A^+ of a selected isotope and unexcited atoms B of another isotope.

The cross section of resonance excitation transfer as slow atoms collide will be /89/:

$$\sigma_{tr} = 2.3 \frac{\tau}{\hbar v} d_{12}^2 , \qquad (3.11)$$

where v is the relative velocity of colliding atoms, d_{12} is the dipole moment of the transition 1-2. For allowed transitions σ_{tr} may be as great as 10^{-13}-10^{-14} cm^2. Under continuous excitation the atoms of a selected isotope are kept in the excited state throughout all the time of their being in the light beam $\tau_{int} = a/v_0$. Let us define the coefficient of ionization selectivity Δ as the ratio between the number of ionized atoms of a selected isotope and the number of ionized atoms of unwanted isotopes. The value $Q = \langle \sigma_{tr} N_0 v \rangle$ determines the rate of resonance excitation transfer to the atoms of unwanted isotopes. Therefore, to obtain the coefficient of ionization selectivity of atoms of a selected isotope Δ the following conditions should be met:

$$(Q\tau_{tr}) \lesssim 1/\Delta \quad \text{or} \quad \Lambda_{tr}/d \gtrsim \Delta \qquad (3.12)$$

where $\Lambda_{tr} = (N_0 \sigma_{tr})^{-1}$ is the free-path length of atoms with respect to excitation transfer. Under pulse excitation, when excited atoms exist in the isotope mixture over a short period of time $\tau < \tau_{int}$ instead of (3.12), not nearly so rigid conditions should be met:

$$(Q\tau) \lesssim 1/\Delta \quad \text{or} \quad \Lambda_{tr}/(\tau v_0) \gtrsim \Delta \qquad (3.13)$$

To cite an example, when the relaxation time of the intermediate level $\tau \simeq 10^{-7}$ sec and the atomic density in a beam $N_0 = 10^{13}$ cm^{-3} the values $\Delta \simeq 10^3$ can be obtained.

The cross-section of resonance ion charge exchange varies between $\sigma_{ch} = 10^{-14}-10^{-15}$ cm^2 with the atomic velocity /89/. Fig. 17 /90/ shows some relations of the kind. The ion produced by selective ionization should be withdrawn from the atomic beam. To obtain the selectivity coefficient S the free-path length of ions with respect to the charge exchange Λ_{ch} and the cross-section of atomic beam d should comply with the condition of type (3.12):

$$\Lambda_{ch}/d \gtrsim S \qquad (3.14)$$

For example, to obtain $S = 10$ with $\sigma_{ch} = 10^{-14}$ cm^2 and d =1 cm this condition imposes a rigid restriction on the overall density of atoms in the beam $N_0 \lesssim 10^{13}$ cm^{-3}. In charge exchange there is practically no momentum exchange. This may be used for suppressing selectivity losses owing to charge exchange in the following manner /75/. If the velocity of the former ions of a selected isotope is increased sharply under the action of a short pulse of electric field so that the ion displacement during the acceleration, d, can be much less than Λ_{ch} (or rather: $d < \Lambda_{ch}/S$) then a subsequent charge exchange will not affect escape of ionized atoms from the beam (now as atoms and not as ions). Spatial separation of ions of a selected isotope at a considerable density can be done in crossed electric and magnetic fields /75/ .It is necessary to use a magnetic field here because of initiation of a space charge, which prevents ions from being removed under the action of electric field only.

Selective ionization of molecules can be accomplished also, as it has been suggested for separating uranium isotopes with UF_6-molecule in one of the earliest works on laser isotope separation /29/. One can selectively excite vibrational molecular level, and due to red shift in the molecular photoionization boundary only excited molecules of a selected isotope can be selectively photoionized. But practically it is difficult to do this because the vibrational shift of photoionization band is small as compared to the red edge width of this band and because there are no suitable lasers in the VUV region for molecular ionization. A certain improvement will be, perhaps, achieved if electronic molecular states are selectively excited and then photoionized, but this approach is applicable only to a small number of molecules which have isotopic shifts in electronic absorption bands.

4. Selective Two-Step Molecular Photodissociation.

The idea of selective two-step molecular photodissociation consists in previous isotope-selective excitation of vibrational or electronic molecular states by laser radiation and in subsequent laser photodissociation of only excited molecules before the excitation is transferred to molecules of other isotopic composition (excitation selectivity loss) and relaxed (Fig. 18a). This idea was conceived as early as in the first work on selective atomic photoionization/22/, then considered and experimentally accomplished in works/23-26/. The process of selective two-step molecular photodissociation is practicable, provided that during molecular excitation a shift in the continuous photoabsorption band occurs which results in molecular photodissociation. In this case, by selecting the radiation frequency ω_2 in the shift area where the ratio between absorption coefficients unexcited and excited molecules is maximum (Fig. 18b), we can realize the photodissociation of the molecules excited selectively by the ω_1-frequency radiation.

In principle, both vibrational and electronic excited states can be used as an intermediate one. Each case has its own pros and cons. As the vibrational state is excited, the shift in the electronic absorption band is rather small sometimes and the low vibrational levels are populated appreciably by nonselective thermal excitation. Therefore sometimes it is difficult to achieve mainly photodissociation of laser-excited molecules. But, on the other hand, isotopic shift shows itself clearly in the vibrational spectrum, as a rule. A rather large shift of photoabsorption band may appear in the electron-excited intermediate state, but electronic spectra of most molecules have no absorption lines with pronounced structures in which isotopic shift shows itself clearly. And, as isotopic structure shows up, the methods of one-step selective photopredissociation (§ 5) and selective electronic photochemistry (§ 7) compete with that of two-step photodissociation. Because of this, the method of selective two-step photodissociation through intermediate vibrational states is of most interest in respect to practice.

The probabilities of excitation and dissociation of excited molecules are given by relations of type (3.2) and (3.6), in which σ_{exc} denotes the excitation cross-section of corresponding intermediate level, and by σ_i is meant the photodissociation cross-section $\sigma_{pt.dis.}$. At the same time in case of molecules the whole picture of selective process is much more complicated due to the following effects governing the selectivity and rate of the process [21]:
1) thermal nonselective excitation of vibrational levels;
2) diffuseness of the band edge of electronic molecular photoabsorption; 3) the effect of "bottle neck" due to rotational structure of vibrational levels. First of all let's consider all these effects.

1) Thermal nonselective excitation of vibrational levels.

Just a small number of thermal molecules should be located at an excited vibrational level, that is:

$$\hbar\omega_1 \gg kT \qquad (4.1)$$

In the simplest case of diatomic molecule, when no more than one half molecules ($N_2^{max} \simeq \frac{1}{2} N_{10}$) may be excited from the ground state under the resonance radiation ω_1 , a more rigid condition should be met so that the coefficient of excitation selectivity $S = N_2/N_{20} \gg 1$ could be obtained:

$$\left(\hbar\omega_1/kT \right) \gg \ln 25 \qquad (4.2)$$

For polyatomic molecules the photodissociation selectivity drops in addition owing to the fact that the levels of one normal vibration are selectively excited by laser radiation, while thermal excitation populates the levels of all normal vibrations, many of which can absorb the photodissociating radiation of ω_2 -frequency as well.

Consideration must be given to the increase in the rate of thermal excitation at the cost of gas mixture heating by IR radiation. This process is illustrated in Fig.19, which shows the time history of population of the first vibrational level of a NH_3-molecule, when gaseous NH_3 under a pressure of 240 torr is acted upon by a pulse of CO_2-laser radiation which leads to absorption saturation at the vibrational transition $v=0 \rightarrow v=1$. Level population is measured by the IR-UV double resonance method /91,57/ Throughout a laser pulse and some time, as long as the vibrational relaxation is small, the population of the level $v=1$ is determined by laser excitation. As the vibrational relaxation proceeds, a gas heating and subsequent thermal excitation of levels with a new much higher gas temperature take place until the gas cools down. Thus, the selective excitation exists only during a rather short period of time (about 1 μsec at NH_3 pressure of some tens of torr), while the thermal nonselective excitation lasts much longer, in the order of msec. In order for selectivity losses of two-step photodissociation due to heating to be eliminated, the ω_2-frequency laser pulse should be also short, no longer than the time of vibration-translation relaxation.

2) Diffuseness of the photoabsorption band edge. Unlike the two-step atomic photoionization where the photoabsorption spectrum edge is sharp, the relation between the shift of electronic absorption band $\Delta\omega_{shift}$ and the red wing edge of this band $\Delta\omega_{wing}$ is essential for the two-step photodissociation. The primary photodissociation of vibration-excited molecules is accomplished only when $\Delta\omega_{shift} \gg \Delta\omega_{wing}$. Fig. 20 illustrates the typical form of continuous absorption bands arising at transitions from the ground and excited vibrational states to a repulsive excited electronic term. The photodissociation band spectrum of a diatomic molecule is given by the formula

$$I_{v\nu} \sim \nu \left| \int_{-\infty}^{\infty} \psi_v(x)\, \psi_\nu(x)\, dx \right|^2, \qquad (4.3)$$

where $\psi_\nu(x)$ is the nuclear wave function of vibrational level of ground electronic state, $\psi_\nu(x)$ is the nuclear wave function of continuous spectrum of excited electronic state.

The absorption band is shifted from the excited state to the red side by the value of vibrational excitation energy, but the band is wider than the shift value, as a rule. For the selective photodissociation it is necessary that there should be a frequency range in which $I_{1\nu} \gg I_{0\nu}$. The estimates show that this is possible only on the red side of absorption band where the photodissociation cross-section decreases sharply.

A rise in the photodissociation selectivity, when the ω_2-frequency is tuned to the far edge of band, results in a decrease in the process rate. Therefore it is advisable to apply other methods for increasing the band shift. High vibrational molecular levels can be directly excited by ω_1-frequency radiation, that is a resonance absorption at vibrational molecular overtones can be used. It was just this way that was applied in the first experiment on two-step photodissociation of HCl-molecule/23/. Work/92/ has demonstrated isotopically-selective excitation of the second overtone of $H^{35}Cl$ and $H^{37}Cl$ molecules with laser radiation at 1.19 μ. In work /93/consideration has been given to the possibility of photodissociation from the higher vibrational molecular levels, populated by molecular vibrational energy exchange as low levels are continuously excited by IR radiation. But collisions result in a loss of isotopic excitation selectivity, that makes no sense in applying the process.

3) The "bottle neck" effect in vibrational level excitation. Due to the Boltzmann distribution of molecules over the

ground vibrational state the monochromatic laser radiation excites just a small portion of molecules q at one rotational sublevel, that decreases the excitation rate. For the excitation rate to be increased, the radiation intensity may be raised. At the same time, if the excitation rate W_{exc} for the molecules at the rotational sublevel of lower vibrational state becomes much higher than that of rotational relaxation $1/\tau_{rot}$, the low sublevel gets depopulated quickly. A further excitation is possible only after the sublevel is populated again owing to rotational relaxation (Fig.21). As a result, the vibrational energy E_{vib} stored up by the molecules under IR resonance radiation complies with the condition [94]:

$$\frac{dE_{vib}}{dt} < \frac{\hbar\omega_1}{2}\,\frac{q}{\tau_{rot}}, \qquad (4.4)$$

where $q \ll 1$ denotes the portion of molecules interacting with the ω_1-frequency radiation directly, τ_{rot} is the time of rotation relaxation. In order that half the molecules be excited by a pulse with its duration τ_p, the condition $\tau_p > \tau_{rot}/q$ should be met. Thus, the characteristic time of vibrational molecular excitation will be:

$$\tau_{exc} = \frac{1}{q}\,\tau_{rot} = \tau_{coll}/P_{rot}\,q, \qquad (4.5)$$

where P_{rot} is the probability of rotational relaxation in one gas-kinetic collision; τ_{coll} is the mean time between gas-kinetic collisions, that is $0.1 < P_{rot} < 1$.

The main restriction on the excitation rate is conditioned by the population factor of vibrational-rotational level q expressed in terms of the statistical sum of rotational states Z_{rot}, the sublevel degeneration g and the energy E_{rot} :

$$q = \frac{g}{Z_{rot}} \exp\left(-\frac{E_{rot}}{kT}\right) \qquad (4.6)$$

For simple molecules the q value can be calculated. Usually it varies between 10^{-1} and 10^{-2}. But for polyatomic molecules, when the levels interacting with radiation are not identified, calculations are impossible. And what is more, sometimes we have to do with a continuous band without an resolved rotational structure but with a distinct isotopic shift (for example, the band ν_3 of $^{10}BCl_3$ and $^{11}BCl_3$ molecules) /95-97/. In this case by the "rotational sublevel" term is meant the very portion of molecules at a vibrational level which resonate with radiation. In all the cases the kind the q value should be measured experimentally. A simple method for measuring the population factor q has been proposed in work /98/. It has been found in this work, for example, that for C_2F_3Cl-molecule and CO_2-laser line at 9.6 μ the factor q = 0.036. The work has shown that the factor q grows with a rise in pressure caused by overlapping of rotational-vibrational lines. The "bottle neck" effect can be revealed as subnanosecond laser pulses are amplified in a CO_2-laser amplifier, where it restricts the rate of extraction of the energy stored in the active medium /99/.

The "bottle neck" effect has influence also on the thermal excitation of levels. Indeed, the value τ_{exc} turns out often to be of the same order with or even more than the vibrational-translational relaxation time $\tau_{V-T} = \tau_{col}/P_{V-T}$ (P_{V-T} is the probability of vibrational excitation relaxation during one collision). Thus, with $P_{V-T} > q\, P_{rot}$ a gas heating becomes inevitable in the process of excitation. The only way to evade it consists in diluting the molecules under excitation with a buffer inert gas, the particles of which when coming into collision result in an efficient rotational relaxation while the vibrational relaxation doesn't increase almost.

The first experiment on isotope separation by the method of two-step selective photodissociation was carried out by R.V.Ambarsumian etc. in their works /26,57/. In their experiments they used $^{14}NH_3$ and $^{15}NH_3$ molecules which, firstly, can be selectively excited by CO_2-laser radiation. Secondly, absorption spectra in the IR and UV regions and photochemical decomposition are well studied as to these molecules. In the region of 10 μ the $^{14}NH_3$ and $^{15}NH_3$ molecules have an absorption band conditioned by the transition $v''=1 \leftarrow v''=0$ in the ν_2 band to a vibrational level with the least energy. The absorption bands of $^{14}NH_3$ and $^{15}NH_3$ overlap but the spectrum has a rich structure consisting of some hundreds of rotational-vibrational lines. This structure has been decoded in work /100/ for $^{14}NH_3$ and in [101] for $^{15}NH_3$. In the spectrum of the ν_2 bands there some non-coincident rotational-vibrational lines of $^{14}NH_3$ and $^{15}NH_3$, yet their frequencies coincide closely with those of CO_2-laser lines. In the UV region the absorption spectrum of $^{14}NH_3$ is an electronic-vibrational progression where a full-symmetric vibration ν_2 shows up, which is active in the IR absorption. The progression starts in the region of 2168 Å and extends to the short-wave region [102]. The electron-excited state $\tilde{A}$ is unstable due to predissociation [103]. Molecular transitions from the ground electron-vibrational state to an excited electronic state and spectral lines arising from such transitions are represented schematically in Fig.22a. For NH_3-molecules vibration-excited to the level $v''=1$ of the band ν_2 the structure of their electronic-vibrational spectrum is somewhat different. The most important thing here is that a new absorption line arises due to the transition $(\tilde{X}, v''=1) \rightarrow (\tilde{A}, v'=0)$. It has a "red" shift the value of which equals to the vibrational quantum energy. When the vibrational transition $v''=1 \leftarrow v''=0$ is fully saturated by IR laser radiation the molecules are equally distributed between the levels $v''=0$ and $v''=1$. Fig.22 b shows a theoretical distribution of intensity in the electron-vibrational spectrum of ammonia absorption for two cases: when all the molecules are in the ground state ($\tilde{X}$, $v''=0$) and when the molecules are equally distributed between the levels $(\tilde{X}, v''=0)$ and $(\tilde{X}, v''=1)$. The new electron-vibrational line at 45250 cm^{-1} has been used in photodissociation of excited molecules.

The experimental scheme, with which the first experiment on isotope separation by the method of two-step photodissociation has been conducted, is schematically given in Fig.21. The CO_2-laser pulse at the line P(16) 10.6 μ excited $^{15}NH_3$-molecules. The CO_2-laser-pulse-ignited spark with a continuous spectrum, the glow duration of which was equal to the duration of IR radiation pulse, was used as a source of UV radiation on the frequency of the new absorption line $(\tilde{X}, v''=1) \rightarrow (\tilde{A}, v'=0)$. An absorbing cell filled with natural NH_3 (99.6% $^{14}NH_3$) was located ahead of the cell with the mixture, in order to remove completely the radiation spark from the continuous spectrum which may be absorbed by unexcited $^{14}NH_3$-and $^{15}NH_3$-molecules. The pressure in the ammonia filter was chosen so that the spark radiation at the transition $(v''=0, \tilde{X}) \rightarrow (v'=0, \tilde{A})$ could be fully absorbed in the filter. Simultaneously with this the light was absorbed at all ammonia transitions with shorter waves. Equimolar mixture of $^{14}NH_3$ and $^{15}NH_3$ at the total pressure of 10-20 torr as well as mixture with a buffer gas (Xe or Ne) at a pressure up to 250 torr were used in the experiment.

The process of ammonia photodissociation comes about according to the scheme [103]:

$$\begin{aligned} &{}^{15}NH_3 + \hbar\omega_1 + \hbar\omega_2 \rightarrow {}^{15}NH_2 + H, \\ &{}^{15}NH_2 + {}^{15}NH_2 \rightarrow {}^{15}N_2H_4, \\ &{}^{15}N_2H_4 + H \rightarrow {}^{15}N_2H_3 + H_2, \\ &2\,{}^{15}N_2H_3 \rightarrow 2\,{}^{15}NH_3 + {}^{15}N_2 \end{aligned} \qquad (4.7)$$

Secondary reactions proceed only between radicals with unexcited $^{14}NH_3$-molecules taking no part in them, that is they are isotope-selective in nature. The mass spectrum of N_2 was analyzed in the experiment. The enrichment coefficient, i.e. the $^{15}N-^{14}N$ content ratio in molecular nitrogen, ranged from 2.5 to 6 in various experiments. In some experiments with molecular oxygen, used as a buffer gas, much a higher enrichment was achieved (up to 50) /104/.

The results of the first experiments on nitrogen isotope separation by the method of two-step photodissociation of NH_3 according to the described scheme have been recently confirmed by Japanese scientists /105/. In their experiment the coefficient of N_2 enrichment with one of isotopes was also 4 at similar conditions.

Some experiments on an analogous scheme (a CO_2 laser and a conventional UV source in the region of 2000 Å) in which the ^{10}B and ^{11}B isotopes were separated through two-step selective photodissociation of BCl_3 molecules are desribed in work /106/. The coefficient of enrichment with a light boron isotope in this work equals only 10% that is comparable to the typical magnitude of kinetic isotope effect. A molecule of O_2 was used as an acceptor of photodissociation products.

Apart from the above-discussed effects of thermal excitation and diffuseness of electronic absorption band the following collisional processes affect the selectivity of isotope separation: 1) the transfer of vibrational excitation as molecules different in isotope composition come into collision; 2) secondary photochemical processes with fragments of dissociated molecules participating.

The transfer of vibrational excitation is a resonance process the probability of which is usually high. For example, the probability of excitation transfer between $H^{35}Cl$ - and $H^{37}Cl$-molecules within one collision will be P_{V-V} =0.1 /107/, while the time of vibrational excitation transfer between $^{14}NH_3$ and $^{15}NH_3$ equals $p\tau_{V-V} = 1.2 \pm 0.4$ nsec.atm. [108]. Thus, for the excitation selectivity to be preserved, the pulse duration τ_{exc} of photodissociating radiation at the ω_2 -frequency should be rather shorter than the excitation transfer time τ_{VV}. The true value of their ratio is determined by the requisite selectivity value S:

$$\tau_{VV}/\tau_{exc} \gtrsim S \qquad (4.8)$$

In the above-discussed experiments with NH_3 this condition was realized by selecting sufficiently short IR and UV radiation pulses (below 10^{-6} sec) and low pressures of NH_3.

Of fundamental importance is the usage of an acceptor which binds photodissociation products without selectivity loss, that is initial undissociated molecules are not drawn into the chemical cycle just as it has been brought about in photodissociating NH_3. The feature of this process is that reactions are practicable with high-energy molecular fragments which can excite molecules of other isotopic composition when colliding with them. Therefore, it is necessary, at least, that the molecular fragments should be thermalyzed before they collide with the initial molecules. Basically, a properly selected acceptor with a sufficiently high pressure can thermalyze molecular fragments, react chemically with them and, what is more, eliminate the "bottle neck" effect thus increasing the rotational relaxation rate.

To accomplish a high-efficiency process of isotope separation by the method under consideration, it is selfevident that the best use of the laser radiation at ω_1 - and ω_2 - frequencies should be made. This problem is complicated by the difference in the cross-sections of excitation σ_{exc} and photodissociation $\sigma_{ph.d.}$, just as in the case of two-step atomic photoionization. But this difference is much less than that in photoionization. Quantitative analysis for the kinetics of two-step molecular photodissociation in a volume has been carried out in work [109]. As stated in this work, given proper parameters it is possible to meet at once the following requirements: 1) photodissociation of a considerable part (at least 50%) of molecules interacting with laser radiation; 2) practically full use of radiation at the both frequencies ω_1 and ω_2.

5. Photopredissociation

Isotope separation by photopredissociation/30,31/requires a molecular excited state which exhibits a resolvable isotope shift, which decays primarily by dissociation, and whose dissociation products

$$AB + h\nu \rightarrow AB^{*} \rightarrow A+B$$

are simply removed from the starting material. The lifetime of the state must be long enough so that lifetime broadening does not cause overlap of the spectra of the two isotopes.

$$\Delta\nu \text{ isotope} >> 1/2\ \pi\tau \qquad (5.1)$$

The reciprocal of τ is the sum of the rates for all decay processes. The quantum yield of dissociation, QY,

$$0<QY=\tau k_{\text{dissociation}} \leq 1 \qquad (5.2)$$

must be large enough to give an acceptable overall process efficiency. To satisfy equation (5.1) lifetimes longer than 10^{-10} or 10^{-11} sec are generally satisfactory. For lifetimes longer than this Doppler broadening will usually limit the selectivity of excitation. Equation (5.2) may be satisfied for much longer lifetimes than 10^{-10} sec. Rate constants for fluorescence emission, inverse radiative lifetimes, usually range from 10^{5} to 10^{8} sec^{-1}. Often dissociation is the only nonradiative decay channel. Thus acceptable values of $k_{\text{dissociation}}$ may range over several orders of magnitude for a particular molecular electronic state. There are a number of molecules with one or more excited states known to satisfy the requirements of Eqs (5.1 and 5.2).

Predissociation may be collision-induced. For example a molecule may be excited to a vibration-rotation level just below a dissociation limit. The spectrum is perfectly sharp since the state is bound but dissociation can be induced with energy from a collision./20,110 /At sufficiently high pressures collision-induced dissociation will compete with spontaneous predissociation./67/Some molecular excited states may be induced to dissociate by the application of modest magnetic or electric fields./111/ In very strong fields shifts in potential curves may introduce curve crossings and hence dissociation pathways./112/For most molecules sufficient spectroscopic and photochemical information is not available to know whether Eq (5.2) is satisfied. It is clear though that the method is not as general as the two-step photoprocesses described in sections 3 and 4.

Photopredissociation has been most extensively studied in formaldehyde/30,67-70,77,113,114/.It is known that near the origin of the first excited singlet state formaldehyde (Fig. 24) dissociates with high quantum yield to H_2 and CO./115/

$$H_2{}^{13}CO + h\nu \rightarrow H_2{}^{13}CO\ (S_1\ v_a) \qquad (5.3)$$

$$H_2{}^{13}CO\ (S_1\ v_a) \rightarrow H_2 + {}^{13}CO \qquad (5.4)$$

$$\rightarrow H_2{}^{13}CO + h\nu^1 \qquad (5.5)$$

Absorption of a single photon leads to chemically stable dissociation products. The rate of fluorescence is much less than the rate of dissociation. Separation of hydrogen from deuterium has been demonstrated using 1:1 mixtures of H_2CO and D_2CO in works /30,67,113,114/. Enrichments, limited by the excitation selectivity of the source, were as high as 9:1 /113/. Recently /116/ an experiment on hydrogen isotope separation in the natural mixture of H_2CO and HDCO has been conducted, where the enrichment coefficient under laser radiation at λ = 32 50.3 Å is about 14. Spectroscopic and photochemical research is underway which should lead to a full understanding of the photo-processes in formaldehyde and to the development of practical systems for the separation of

^{13}C, ^{18}O and ^{17}O. Recently in work /117/ 80-fold enrichment of CO in isotope ^{12}C has been obtained by means of photopredissociation of a mixture $^{12}CH_2O$: $^{13}CH_2O$ = 1:10.

Spectroscopic limitations on the selectivity of excitation were discussed in section 2. An additional set of limitations is imposed by the complexity of formaldehyde photochemistry. Spontaneous predissociation to molecular fragments (5.4) may be accompanied by the production of free radicals.

$$H_2{}^{13}CO(S_1\ v_a) \rightarrow H + H^{13}CO \qquad (5.6)$$

Large quenching cross sections have been observed for excited formaldehyde. These collisions yield dissociation products,

$$H_2{}^{13}CO\ (S_1\ v_a) + M \rightarrow H_2 + {}^{13}CO + M \qquad (5.7)$$

$$\rightarrow H + H^{13}CO + M \qquad (5.8)$$

$$\rightarrow H_2{}^{13}CO\ (S_1\ v_b) \qquad (5.9)$$

and possibly reaction products.

$$H_2{}^{13}CO(S_1\ v_a) + H_2CO \rightarrow H_2{}^{13}COH + HCO \qquad (5.10)$$

Triplet state formaldehyde may also be produced/118/.Free radical dissociation products react chemically and degrade the isotopic selectivity,

$$H + H_2CO \rightarrow H_2 + HCO \qquad (5.11)$$

$$2HCO \rightarrow H_2 + 2CO \qquad (5.12)$$

unless effective radical scavengers are added. (5.13)

$$H + HI \rightarrow H_2 + I \qquad (5.13)$$

$$HCO + HI \rightarrow H_2 + CO + I \qquad (5.14)$$

$$I + HCO \rightarrow HI + CO \qquad (5.15)$$

Isotopic selectivity is also degraded by energy transfer

$$H_2{}^{13}CO\ (S_1\ v_a) + H_2CO \rightarrow H_2{}^{13}CO + H_2CO\ (S_1 v_c) \qquad (5.16)$$

$$\rightarrow H_2{}^{13}CO + H_2 + CO \qquad (5.17)$$

$$\rightarrow H_2{}^{13}CO + H + HCO \qquad (5.18)$$

The degradation by free radical and energy transfer processes 5.10, 5.11, 5.16-5.18, is especially serious when very high purities of a rare isotope are desired. For example, if processes proceed at 10% the rate of (5.4 and 5.7) then a maximum of 90% purity can be achieved in a 1-step enrichment process. If the spectroscopic selectivity is adequate only for 50% product purity (e.g. ^{13}C enriched from 1.1%), the radical reactions and energy transfer would only degrade the product to a 45% purity.

Isotopically selective photochemistry has been demonstrated by Leone and Moore[116] for bromine. Br_2 is selectively excited to levels of the $^3\Pi_{o^+u}$ state. (Fig. 25). The excited molecules dissociate and the reactive isotopically selected atoms produced are scavenged by HI to yield isotopically enriched HBr. The enriched HBr was identified by its infrared chemiluminescence but not actually separated from the gas flow.

The Br_2 spectrum is sufficiently well-resolved with a 1.2 GHz laser bandwidth at 558 nm that fluorescence of each of the three isotopic molecules, $^{79,79}Br_2$, $^{81,81}Br_2$ and $^{79,81}Br_2$, may be selectively excited as the laser is tuned. The presence of continuum absorption along with the banded spectrum at 558 nm is shown by the fact that Br atoms are produced at wavelengths for which no fluorescence is observed. At 558nm 40% of the absorption was due to the continuum and at 532 nm 80%. Since the Doppler width is about 0.5 GHz a higher resolution laser would give larger line absorption. The continuum absorption gives no isotopic selection

$$^nBr_2 + h\nu \longrightarrow {}^iBr_2^* \quad \text{banded}$$

$$\longrightarrow 2\ {}^nBr \quad \text{continuum}$$

Fluorescence spectra with a 1 GHz resolution dye laser (Molectron) revealed no improved line-to-continuum ratios at longer wavelengths. /120/ The peak absorption cross sections for normal gas at room temperature near 558 nm are about $10^{-19}\mathrm{cm}^2$. Excitation of the $^3\Pi_{1u}$ state slightly below its dissociation limit would completely eliminate the problem of continuum absorption. The excited molecules could be dissociated by collisions. Unfortunately, this absorption spectrum is very weak.

The excited Br_2 molecules may decay by several paths./120/

$$^{i}Br_2^* \longrightarrow {}^{i}Br_2 + h\nu \qquad (\tau_{rad}=\text{a few } \mu\text{sec}) \qquad (5.19)$$

$$\longrightarrow {}^{i}Br + {}^{i}Br \qquad (k\sim 10^6\text{-}10^7\ \mathrm{sec}^{-1}) \qquad (5.20)$$

$$^{i}Br_2^* + M \longrightarrow {}^{i}Br + {}^{i}Br + M (\sigma\sim 10^{-14}\ \mathrm{cm}^2) \qquad (5.21)$$

$$\longrightarrow {}^{i}Br_2 + M \qquad (\sigma < 10^{-14}\ \mathrm{cm}^2) \qquad (5.22)$$

They may also transfer energy to Br_2 collision partners

$$^{i}Br_2^* + {}^{n}Br_2 \longrightarrow {}^{i}Br_2 + {}^{n}Br_2^* \qquad (5.23)$$

with a resulting loss of isotopic selectivity. This is probably not an important problem here because Br_2^* decays much more rapidly than Br atoms react and because (5.21) is probably faster than (5.23). It is important to know the rates of all of these competing processes in order to establish the optimum pressures of Br_2, HI and possible inert gases.

For the atoms there are two competing processes.

$$ {}^{i}Br + HI \longrightarrow H^{i}Br + I \ (k=1.0\times10^{-11}\ cm^{3}\ molec^{-1}sec^{-1})^{118} \tag{5.24}$$

$$ {}^{i}Br + {}^{n}Br_{2} \longrightarrow {}^{i}Br^{n}Br + {}^{n}Br \ (k=5\times10^{-11}) \tag{5.25}$$

The ratio of these two rate constants and the desired purity of the product determine how large the ratio of HI to Br_2 is needed. Measurements of HBr enrichment as a function of the HI:Br_2 ratio indicate that Br + Br_2 is faster than Br + HI by roughly a factor of 5.[120] Direct measurement of the Br + HI rate gives reaction once in every 16 collisions.[121] Were it not for this very fast scavenger reaction rate the isotopic selectivity of the excitation would be lost.

The disadvantage of these highly reactive chemical systems is that undesired side reactions may proceed at rates sufficient to scramble the isotope selection before the final physical isolation of the chemical products is carried out. In this system for example the reactions

$$Br_2 + HI \longrightarrow HBr + BrI \tag{5.26}$$

$$BrI + HI \longrightarrow HBr + I_2 \tag{5.27}$$

appear to proceed rapidly on the walls of the vessel. The I atoms produced (5.24) react with Br_2

$$I + {}^{n}Br_{2} \longrightarrow 1^{n}Br + {}^{n}Br \tag{5.28}$$

less rapidly than once in each 10^3 collisions. If the separation may be carried out in a fast flow system with walls sufficiently cold that Br_2 and I are trapped, it should be possible to collect the $H^{i}Br$. For such a system to work efficiently the product of Br_2 absorption cross section ($\sigma \sim 10^{-19}$ cm^2) times pressure times path length must approach unity for efficient use of photons. The laser power must be high enough to excite a substantial fraction of the molecules so that trace impurities and non-selectively produced HBr are not the main product collected.

By selective predissociation of ortho-I_2 molecules with 514.5nm argon ion laser light authors of work/122/ were able to convert ortho to para-I_2. At the operating pressure of 0.25 torr the following processes occurred

$$o\text{-}I_2 + h\nu_{\text{laser}} \longrightarrow o\text{-}I_2^* \qquad (5.29)$$

$$o\text{-}I_2^* + I_2 \longrightarrow I + I + I_2 \qquad (5.30) \quad {}^{123}$$

$$I + I + I_2 \longrightarrow o\text{-}I_2 + I_2 \qquad (5.31)$$

$$\longrightarrow p\text{-}I_2 + I_2 \qquad (5.32)$$

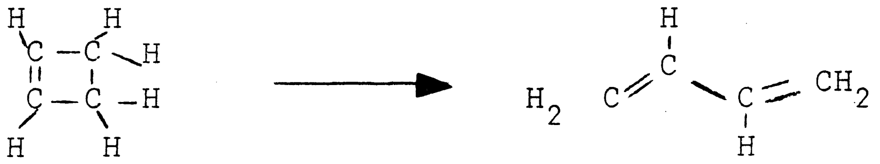
Since (5.29) + (5.30) destroys only $o\text{-}I_2$ and since recombination produces equilibrium amounts of ortho and para (equilibrium ratio $o\text{-}I_2 : p\text{-}I_2 = 7:5$), the gas is enriched in $p\text{-}I_2$. The system reached a steady state in several tens of minutes. Beyond this time reconversion and laser selection proceeded with equal rates. The extent of conversion at steady state increased with laser power. It is likely that collisions between I atoms and I_2 caused o-p conversion. The kinetics of photophysical processes during selective excitation of ortho-I_2 by laser radiation has been studied in more detail lately in work /124/. This work shows that the inverse conversion of para -I_2 to ortho-I_2 occurs with the complex of I_3 formed. The typical time dependence of kinetics of decrease in concentrations of ortho-I_2 and para - I_2under radiation is drawn in Fig.26. With the iodine vapour pressure of 5 m Torr and the laser power of 2.2 W the enrichment coefficient was equal to 2. With increasing pressure it was decreased drastically. Studies on the kinetics of enrichment show that enrichment is governed by conversion on wall-adsorbed iodine atoms. The dependence of enrichment on radiation time and pressure has made it possible to construct the model and to find the rates of the principal processes: recombination probability of iodine atoms on the cell walls $\delta = (1.04 \pm 0.07)\ \mathrm{sec}^{-1}$, desorption probability $K^* = (2.3 \pm 0.25)\cdot 10^{-4}\ \mathrm{sec}^{-1}$, conversion rate constant $\beta = (1.88 \quad 0.09)\cdot 10^{16}\ \mathrm{cm}^6\ \mathrm{mol}^{-2}\ \mathrm{sec}^{-1}$, quantum yield of predissociation from the excited state $B^3\Pi_{0+u}$ with $v = 43$ of a I_2 molecule $\gamma = 1.66\cdot 10^{-5}$. The enrichment factor can be enhanced by choosing a vessel material, which adsorbs atoms at a slow rate, or adding a reagent which binds excited molecules. The last method will be described in detail below, in § 7. Clearly, when radiation source is tunable dye laser it is possible to separate I isotopes.

There are other molecules where predissociation might be used for isotope separation. NH_3 exhibits a predissociated spectrum near 210 nm.[125] Some transitions in ICl are known to be predissociated. Although spontaneous predissociation of states exhibiting well-resolved spectra may be relatively rare, it can be expected that collision-induced predissociation is a more general phenomenon. Collisional quenching of states with energy in excess of the threshold for dissociation to ground state products is very likely to proceed by dissociation.

The dissociation of high vibrational levels of ground electronic state molecules is yet another possibility. After all, thermally induced dissociation proceeds via collisional excitation of vibrations until the dissociation threshold is passed. The molecule, HN_3, is reported to exhibit line broadening in the v=3 and v=4 levels of the hydrogen stretching vibration.[126] If this is so, selective dissociation of ^{15}N molecules should be possible with an infrared dye laser. The very small absorption cross sections for high overtone transitions present a serious problem in practice. However, successful experiments on isotopically-selective excitation of second overtone HCl have been performed in work /92/. Several carefully chosen infrared photons might be used instead for a stepwise or simultaneous multiphoton absorption. (see also section §6). As with electronically excited states it may also be useful with vibrationally excited states to use collisions to assist in the dissociation process. Molecules which will be dissociated by absorption of a small number of vibrational quanta will naturally be ones like HN_3 which are somewhat thermally unstable and therefore dangerous to handle in large quantities.

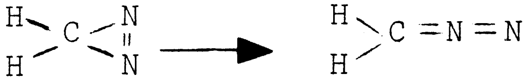
If sufficiently short wavelength photons are available, it may be possible to excite autoionizing levels of atoms and molecules.

A process closely related to photopredissociation is that of unimolecular isomerization./57,127/ A rearrangement of chemical bonds such as


(5.33)

renders products which are quite easily separated from stating material.

Unfortunately most molecules for which such processes have been studied are too large and complex to be likely to exhibit well-resolved isotopic shifts.[128] By suspending the molecule to be excited in a low temperature matrix the spectrum may be simplified by removing the rotational structure and the possibility of dissociation diminished by confining the fragments in the matrix cage. The photochemical transformation



(5.34)

was carried out in this way.[129] Predissociation might also be carried out in a matrix.

Photopredissociation promises to become a practical method of isotope separation. Work on formaldehyde may lead to economically viable methods of enriching ^{13}C, ^{14}C, ^{17}O and ^{18}O. While the method is not as generally applicable as the two-photon methods, it may be considerably less expensive in those situations where it can be used.

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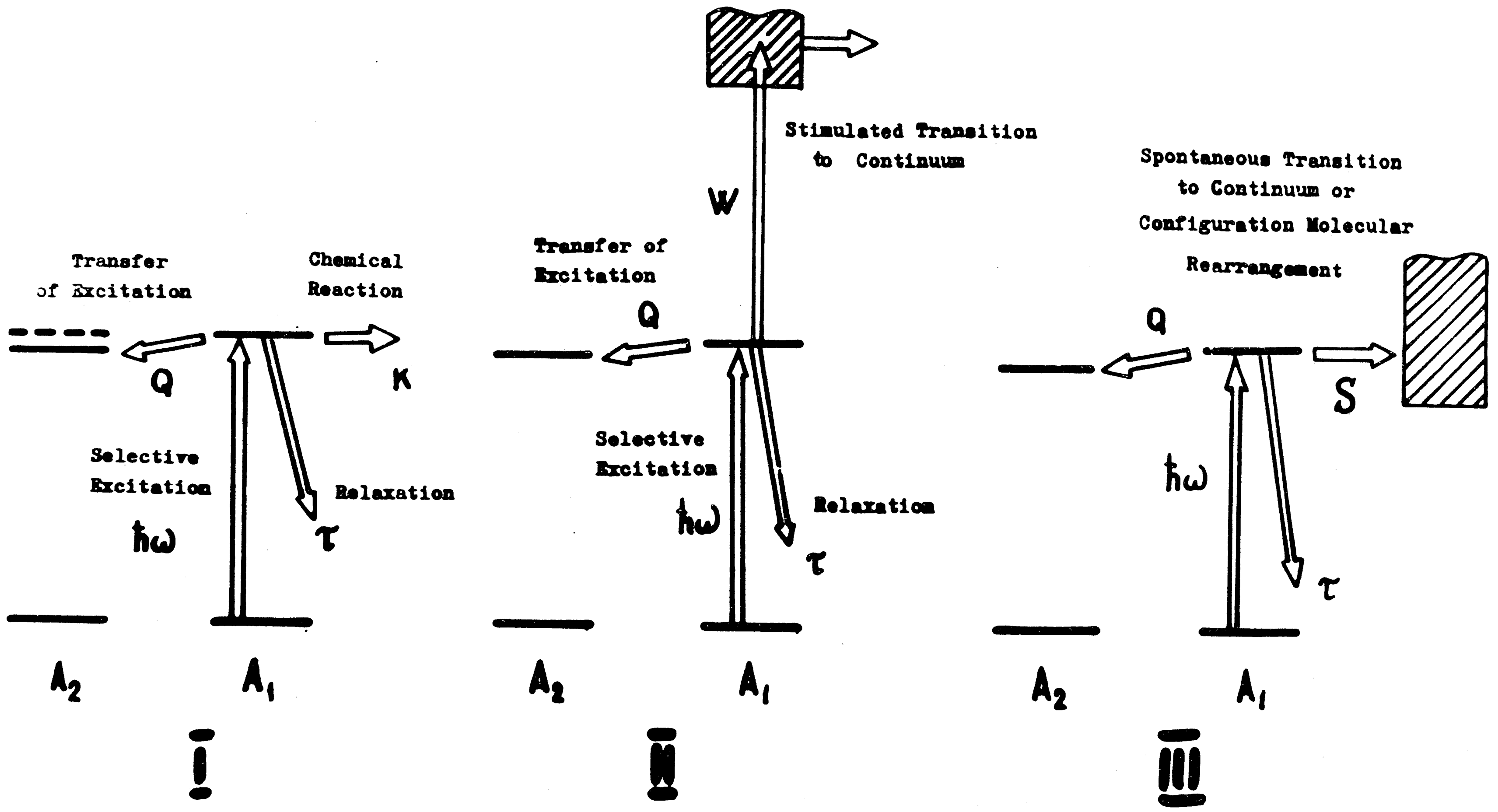
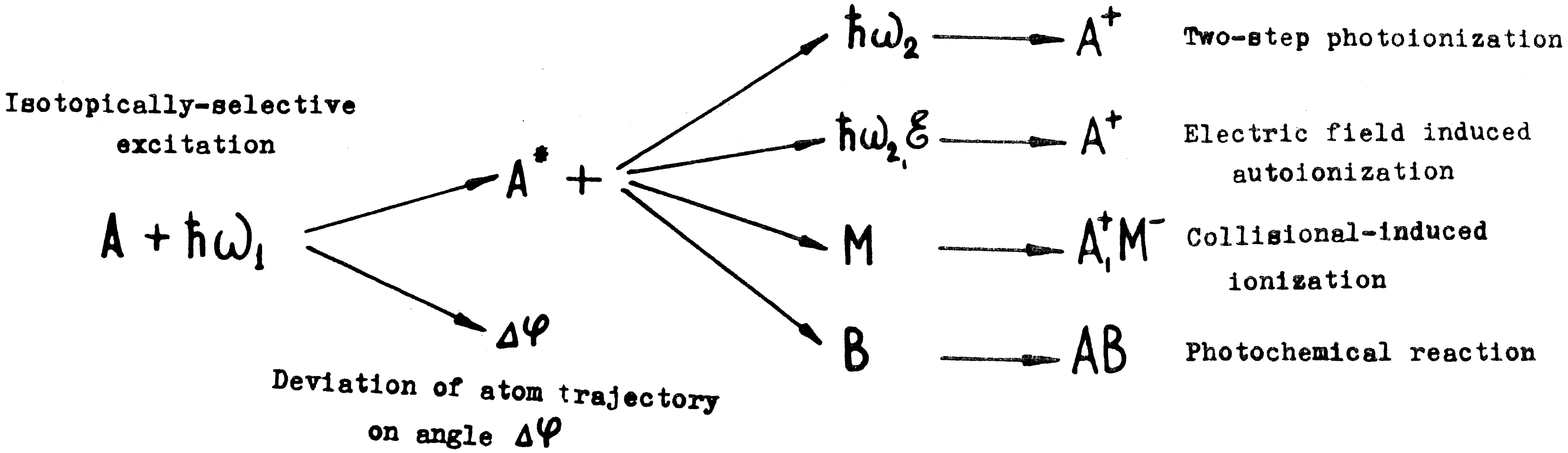


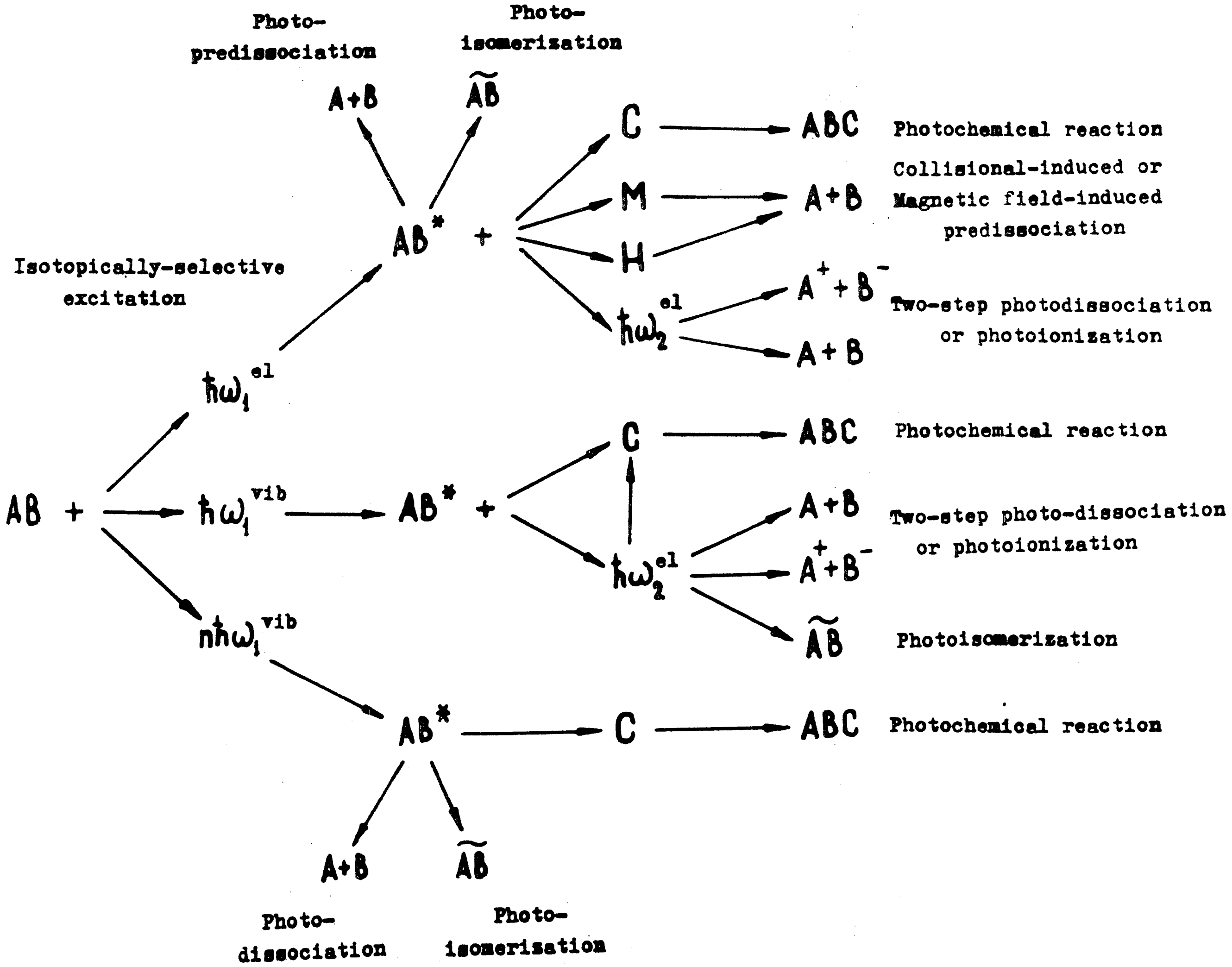
XBL 763-831

Fig. 1. Comparison between the photochemical (I) and photophysical (II,III) processes of selective action of laser radiation on A_1 molecules mixed with A_2 molecules (I-chemical reaction of excited molecules, II - selective photodissociation, III - selective photopredissociation or photoisomerization).



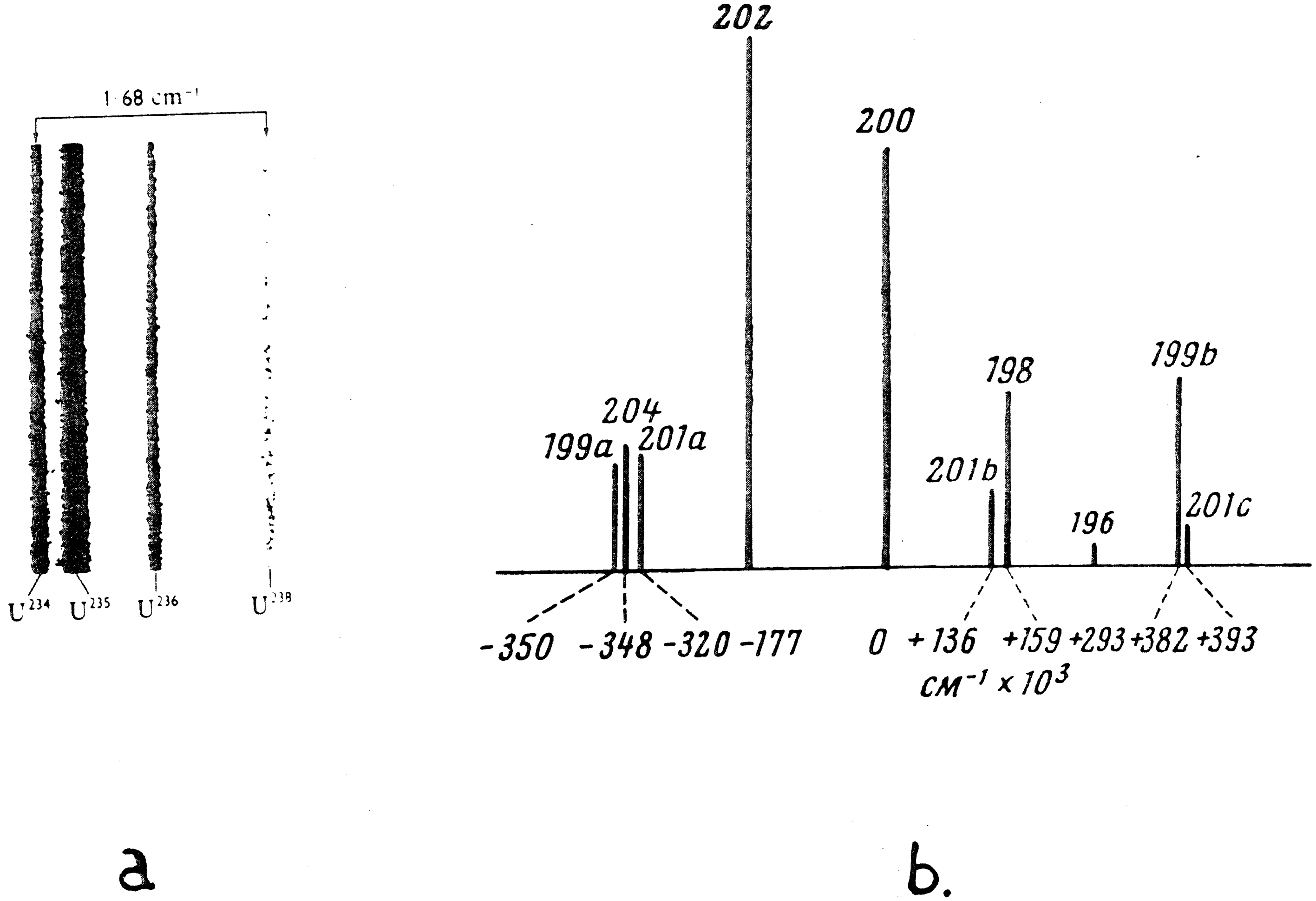
XBL 763-832

Fig. 2. Possiblė schemes of laser isotope separation based on selective action on atoms.



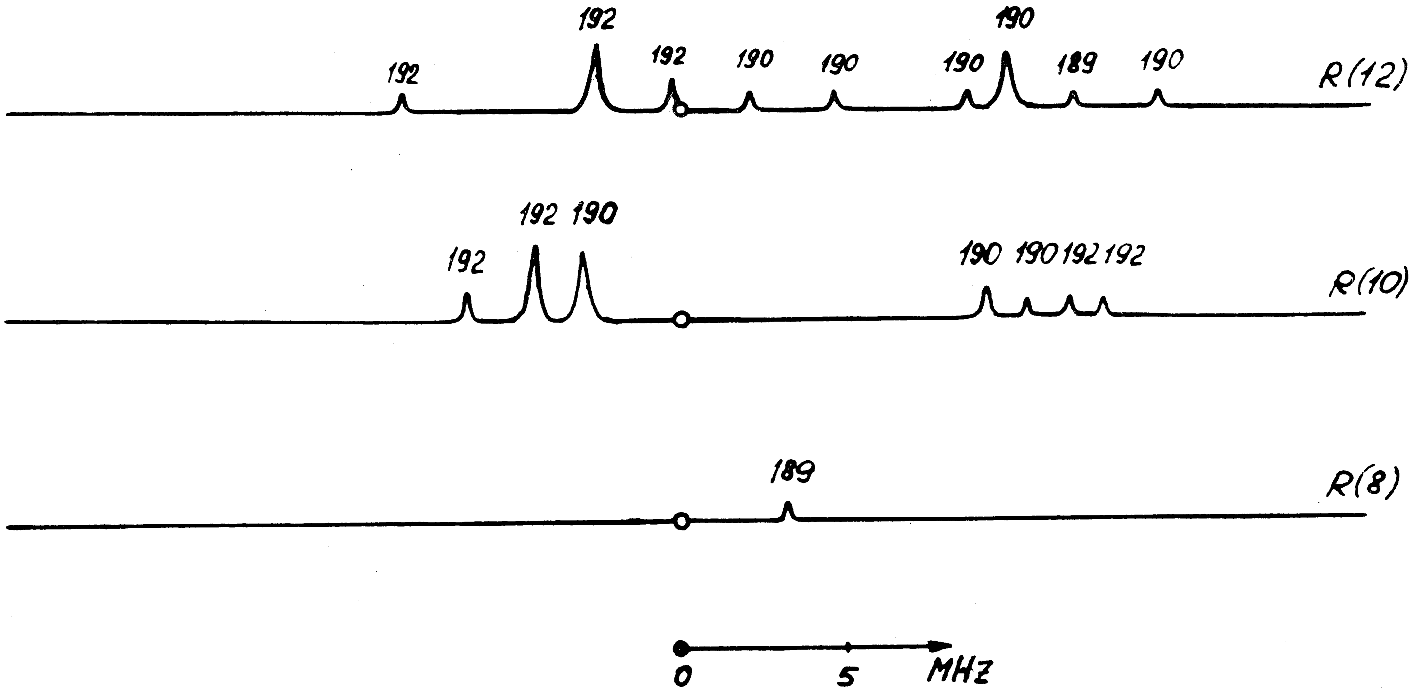
XBL 763-833

Fig. 3. Possible schemes of laser isotope separation based on selective action on molecules.



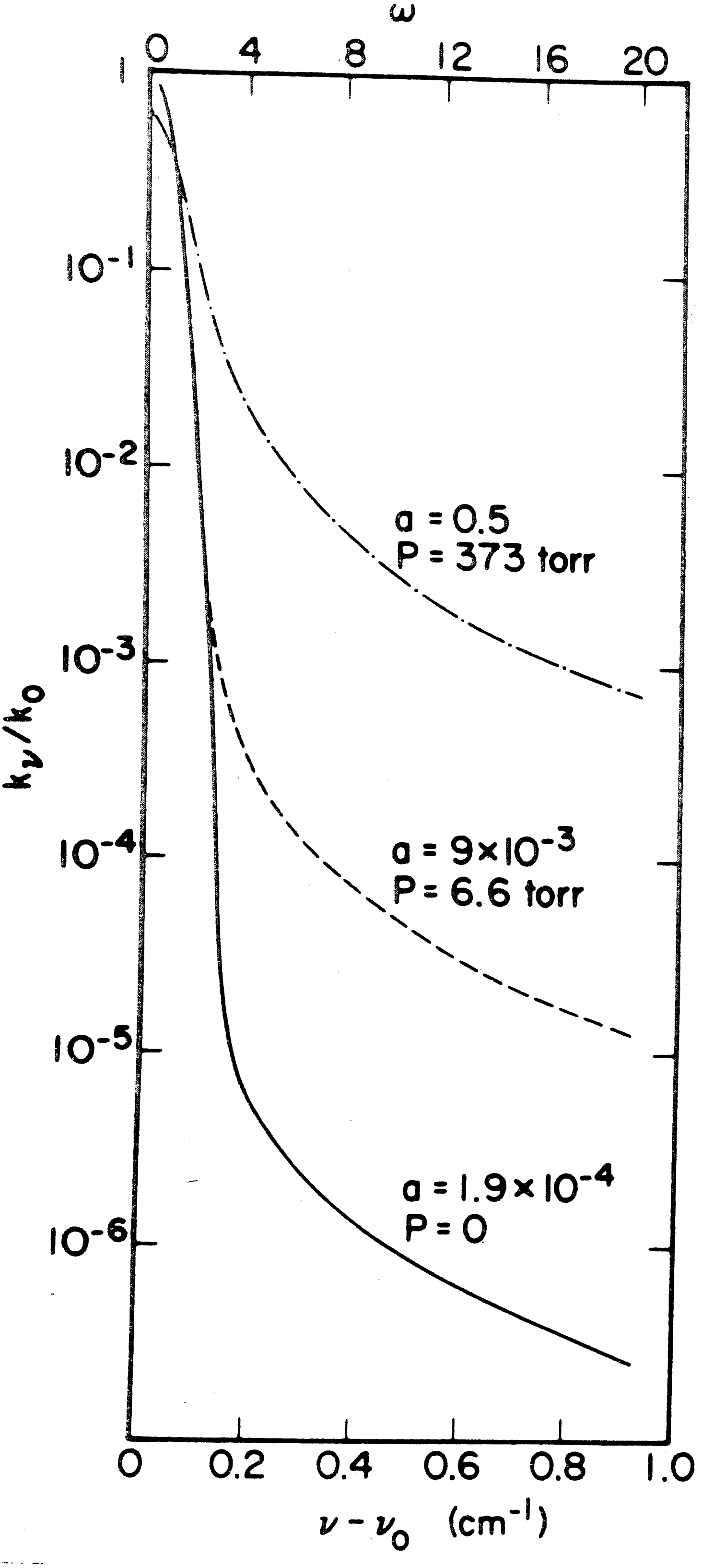
XBL 763-834

Fig. 4. The isotope structure of the line 4244.4 Å UII (a) and the isotope and hyperfine structures of the line 2537 Å Hg I (b).



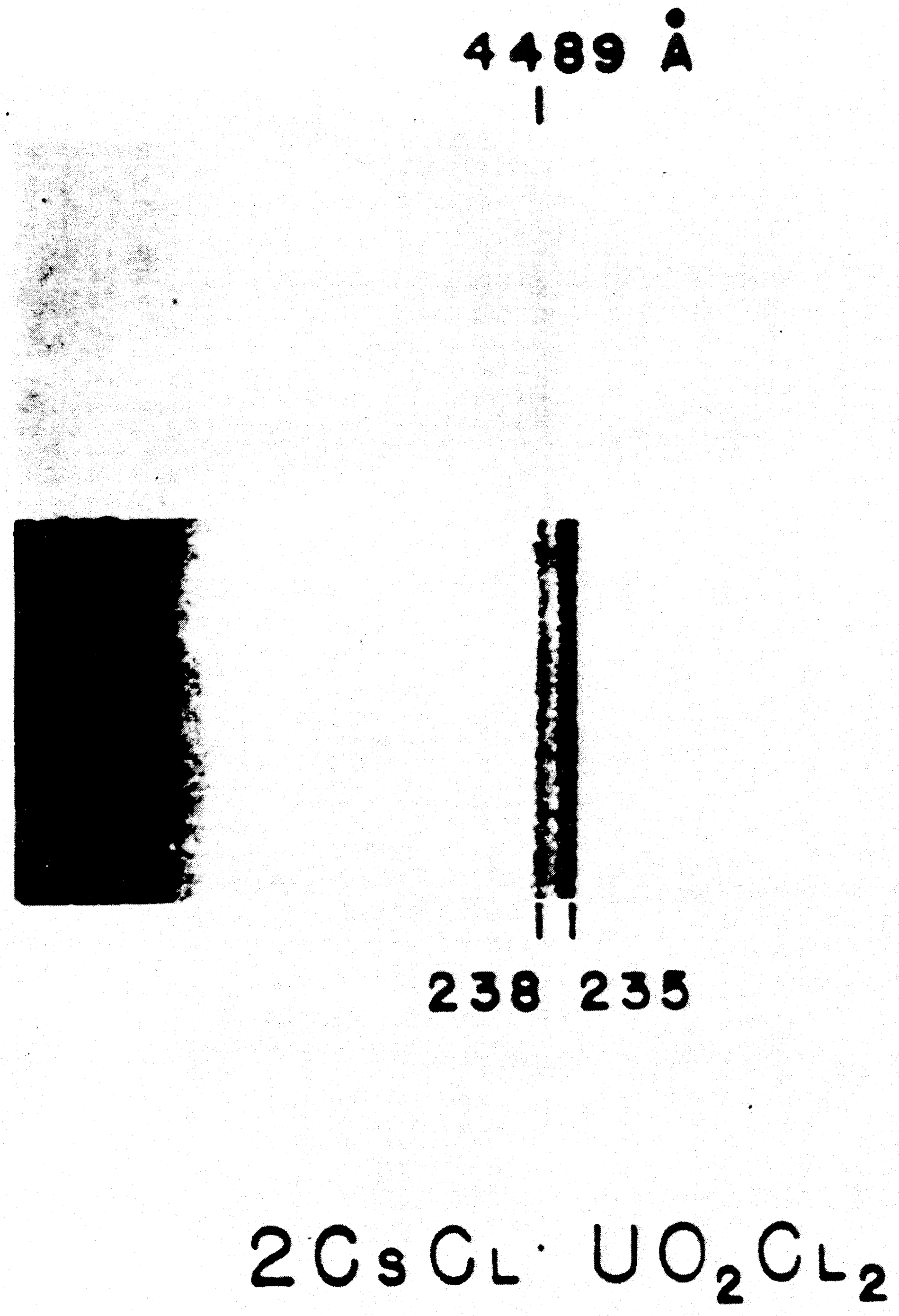
XBL 763-835

Fig. 5. The vibrational-rotational spectrum of saturated absorption without Doppler broadening of OsO_4 monoisotopic molecules in the frequency tuning region of R(8) - R(12) lines of a CO_2 laser (data from work /42/).



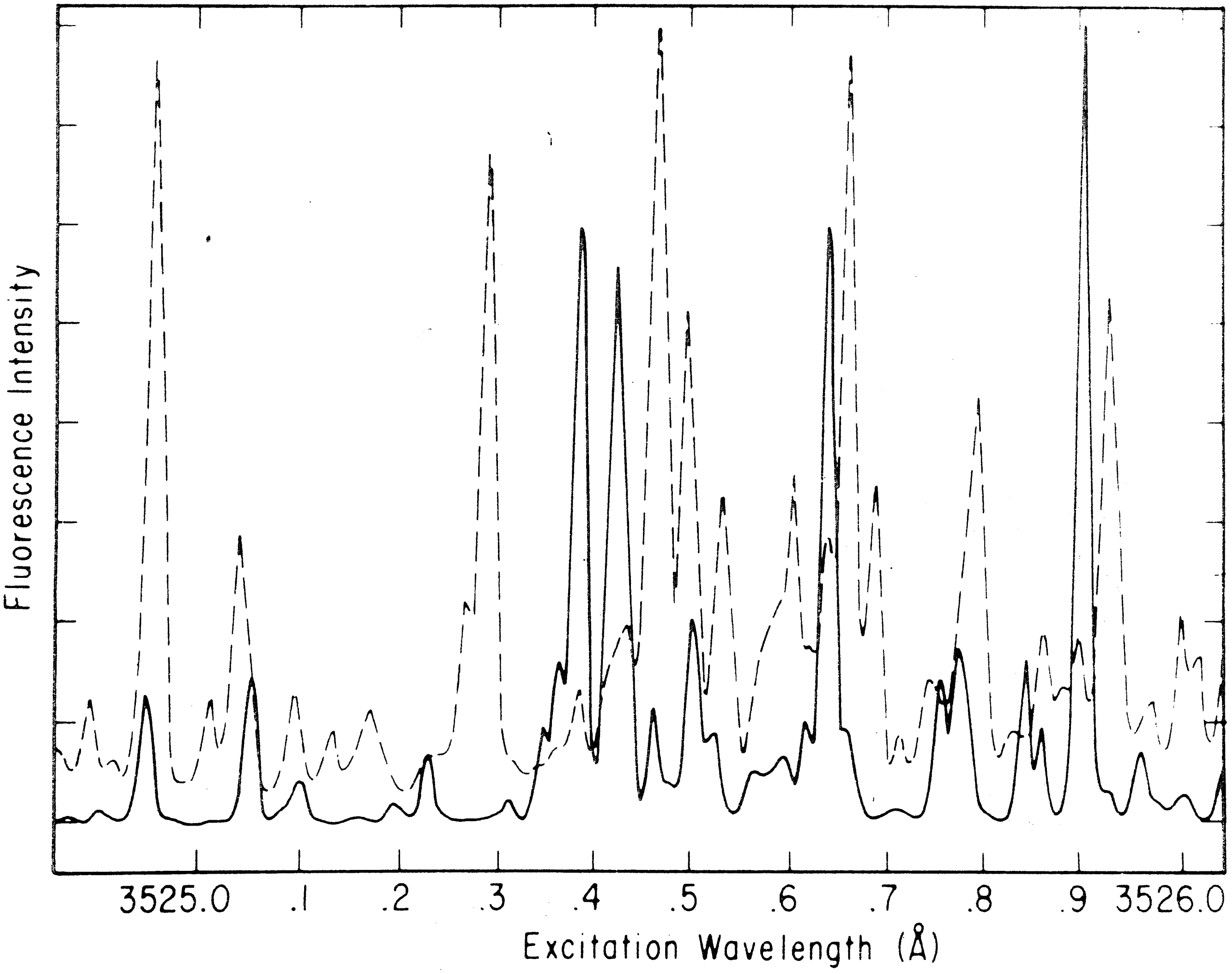
XBL 763-836

Fig. 6. The profiles of H_2CO absorption lines in the region of 3500 Å showing combined Doppler and Lorentzian broadening at various pressures of formaldehyde (Ko is the maximum absorption coefficient for the case of Doppler broadening, a = $\sqrt{\ln 2}\,\frac{\Delta\nu_L}{\Delta\nu_D}$ is the dimensionless parameter which characterizes the value of Lorentzian and Doppler broadening, $\Delta\nu_L \simeq$ 20 MHz/torr) (from work /36/).



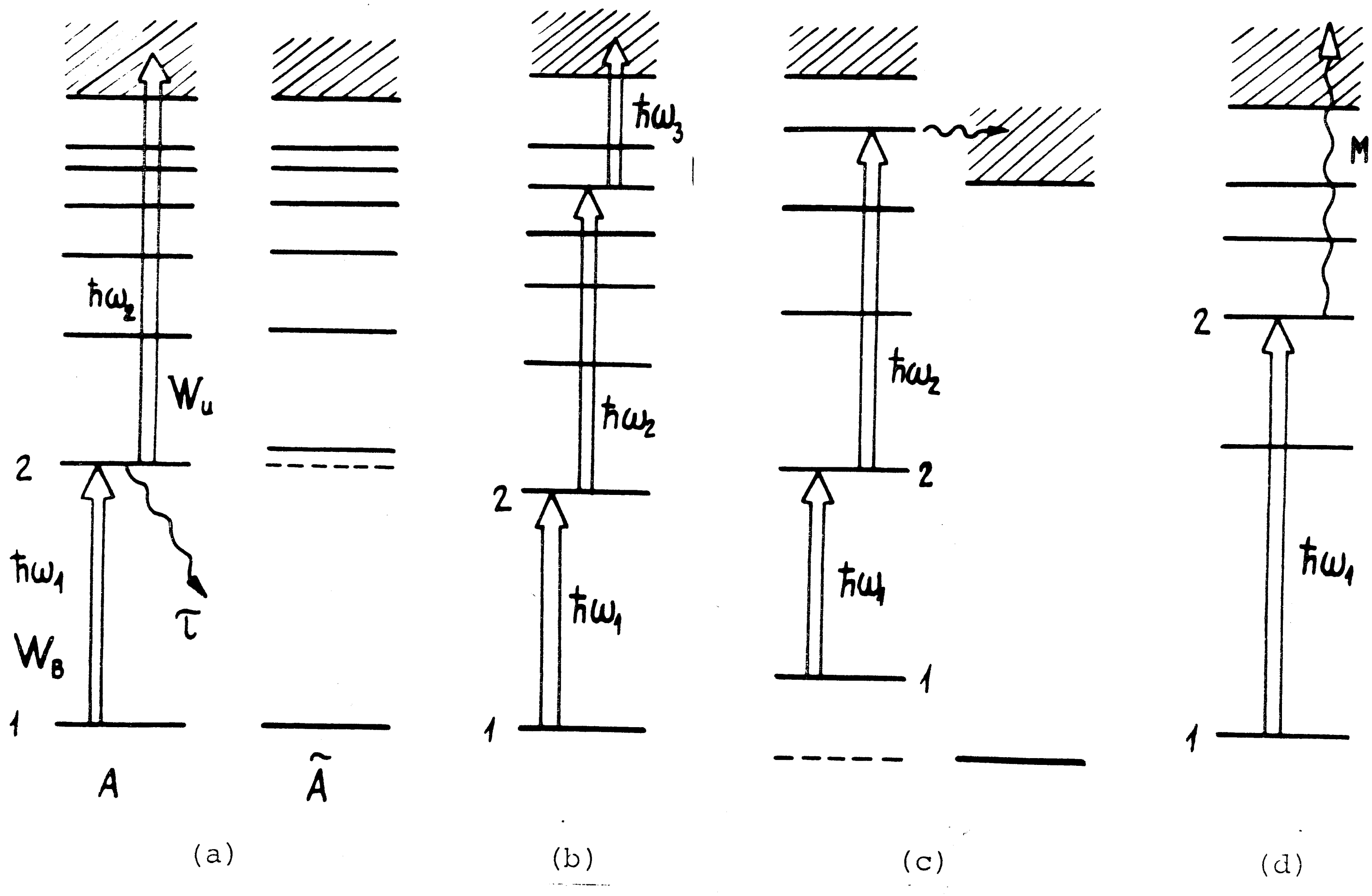
XBB 763-2296

Fig. 7. The isotope structure of the absorption line 4489 Å of the uranium compound 2 $CsCl \cdot UO_2Cl_2$ at low temperature (from work /53/).



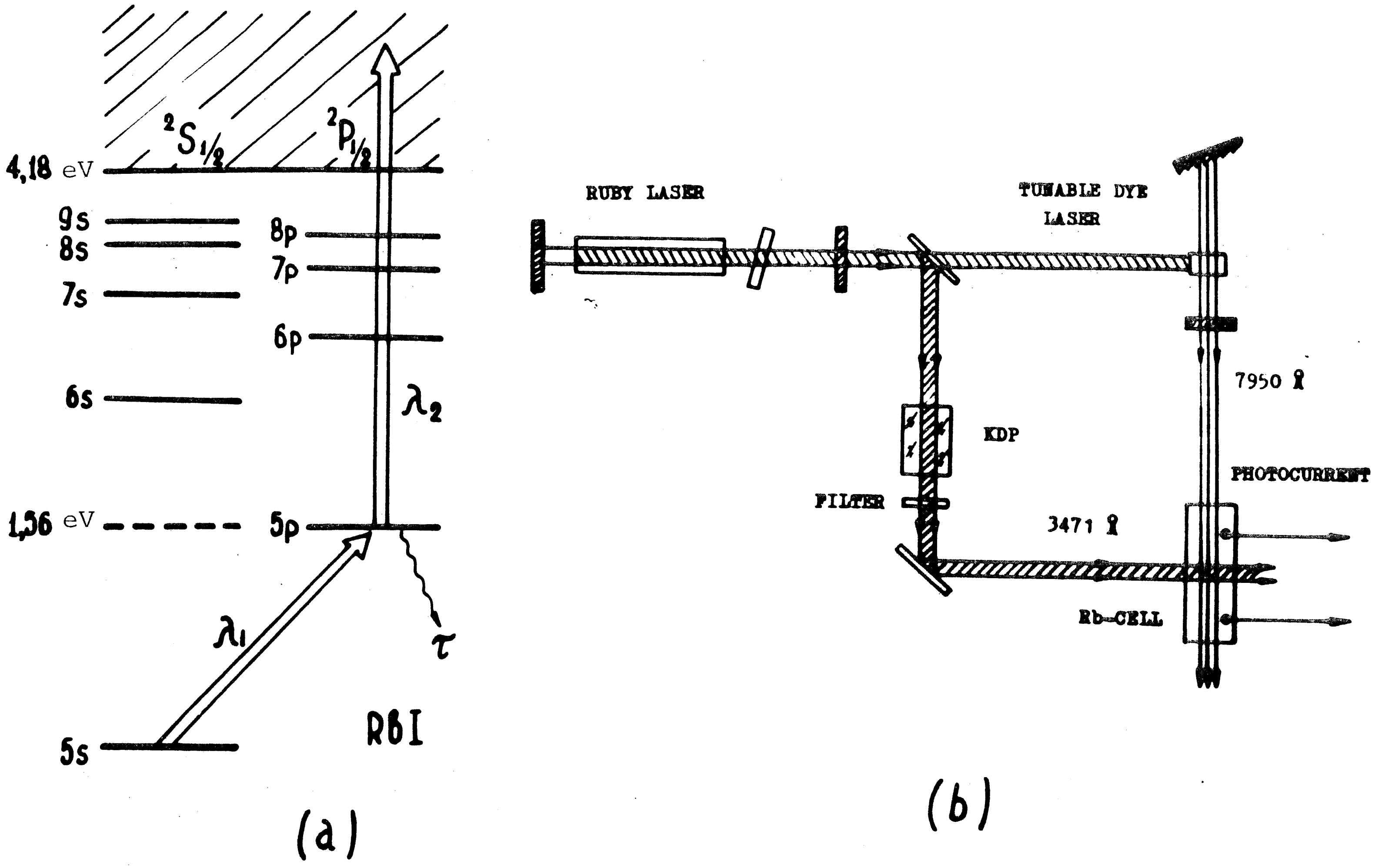
XBL 763-838

Fig. 8. Part of the fluorescence excitation spectrum of $H_2{}^{12}CO$ (-) and $H_2{}^{13}CO$ (----) molecules obtained by scanning the frequency of a pulse dye laser (from /68/).



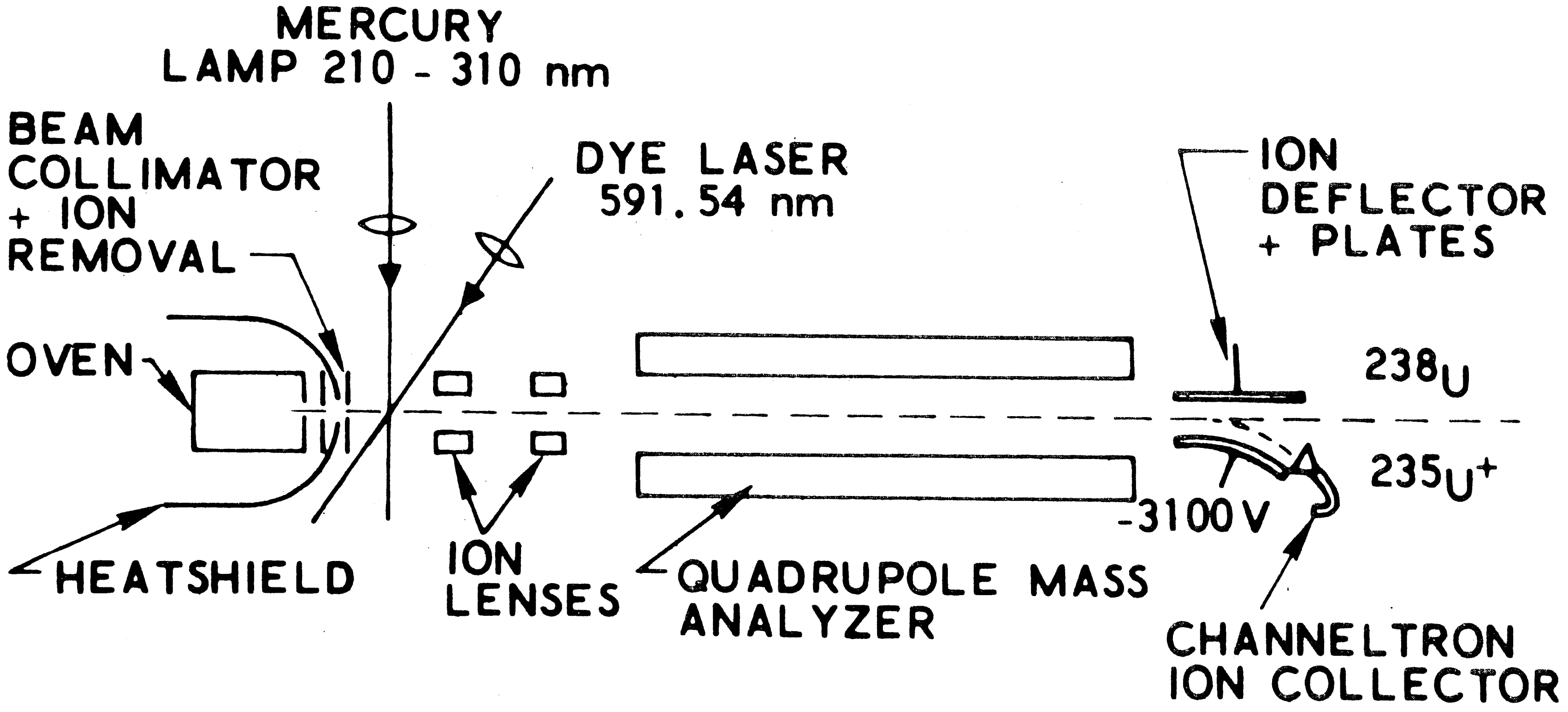
XBL 763-839

Fig. 9. Schemes of selective atomic photoionization by laser radiation; a) two-step photoionization; b) three-step photoionization; c) two-step photoionization through autoionization state; d) ionization during collision of an excited atom with another particle.



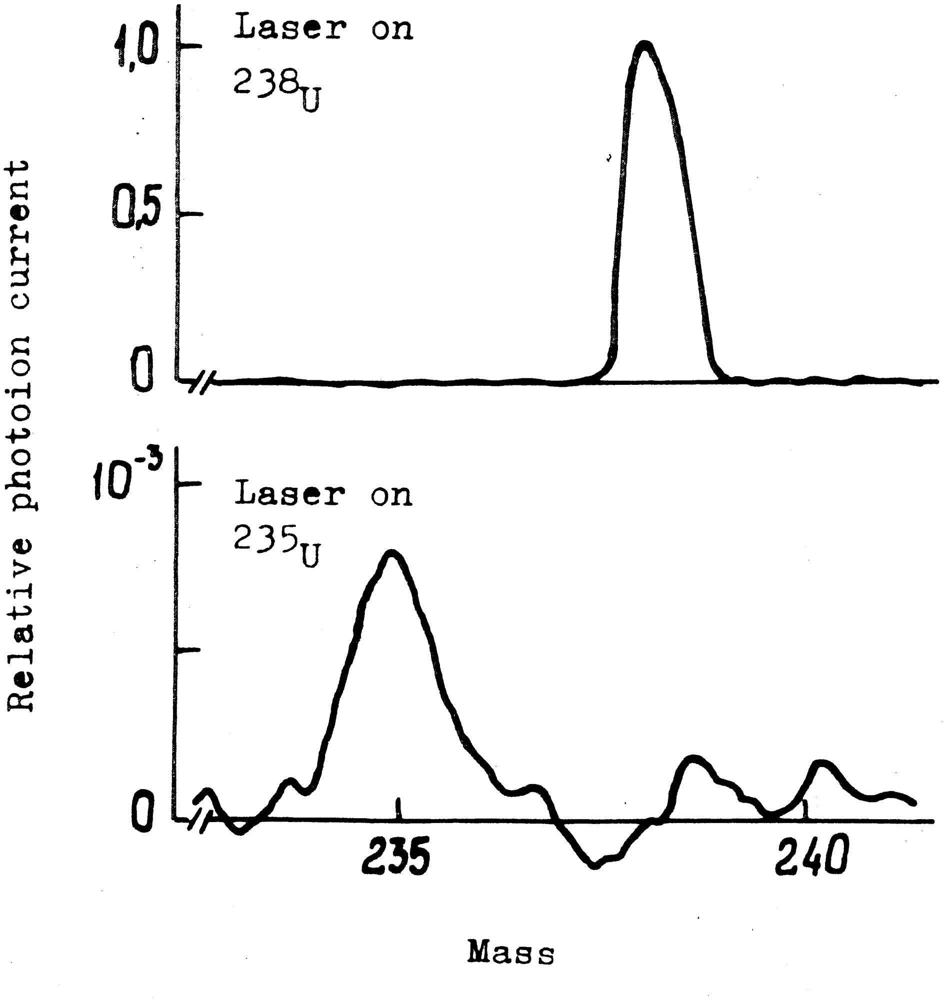
XBL 763-840

Fig. 10. Selective two-step photoionization of Rb atoms: a) level and transition scheme; b) scheme of the first experiment carried out in work /22/.



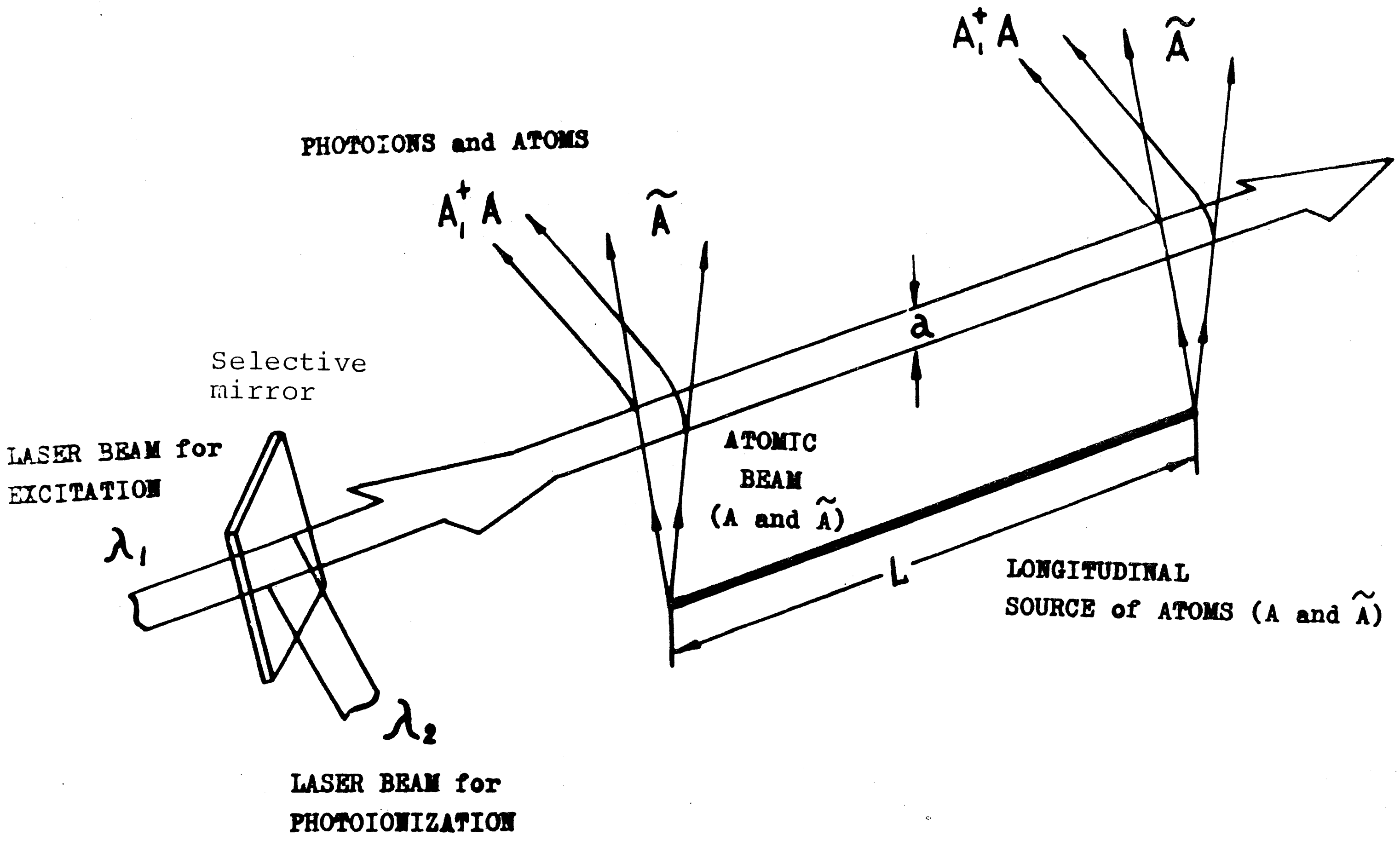
XBL 763-841

Fig. 11. The experimental scheme for indicated separation of U-235 U-238 isotopes through two-step photoionization of uranium atoms in a beam (from /80/).



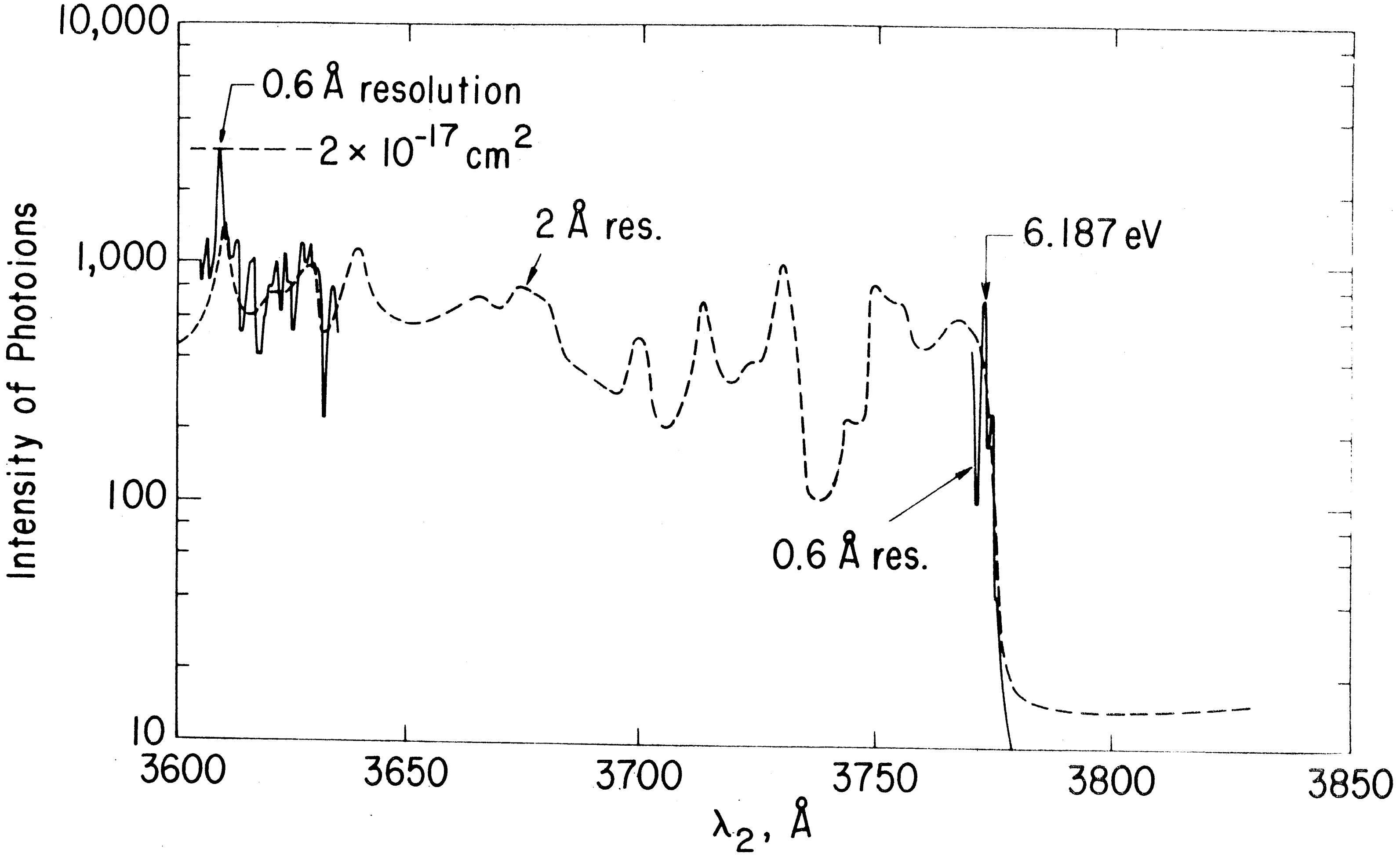
XBL 763-842

Fig. 12. The mass spectrum of uranium ions in selective laser excitation and ionization of U - 238 (up) and U - 235 atoms (down) in the natural isotope mixture (from /80/).



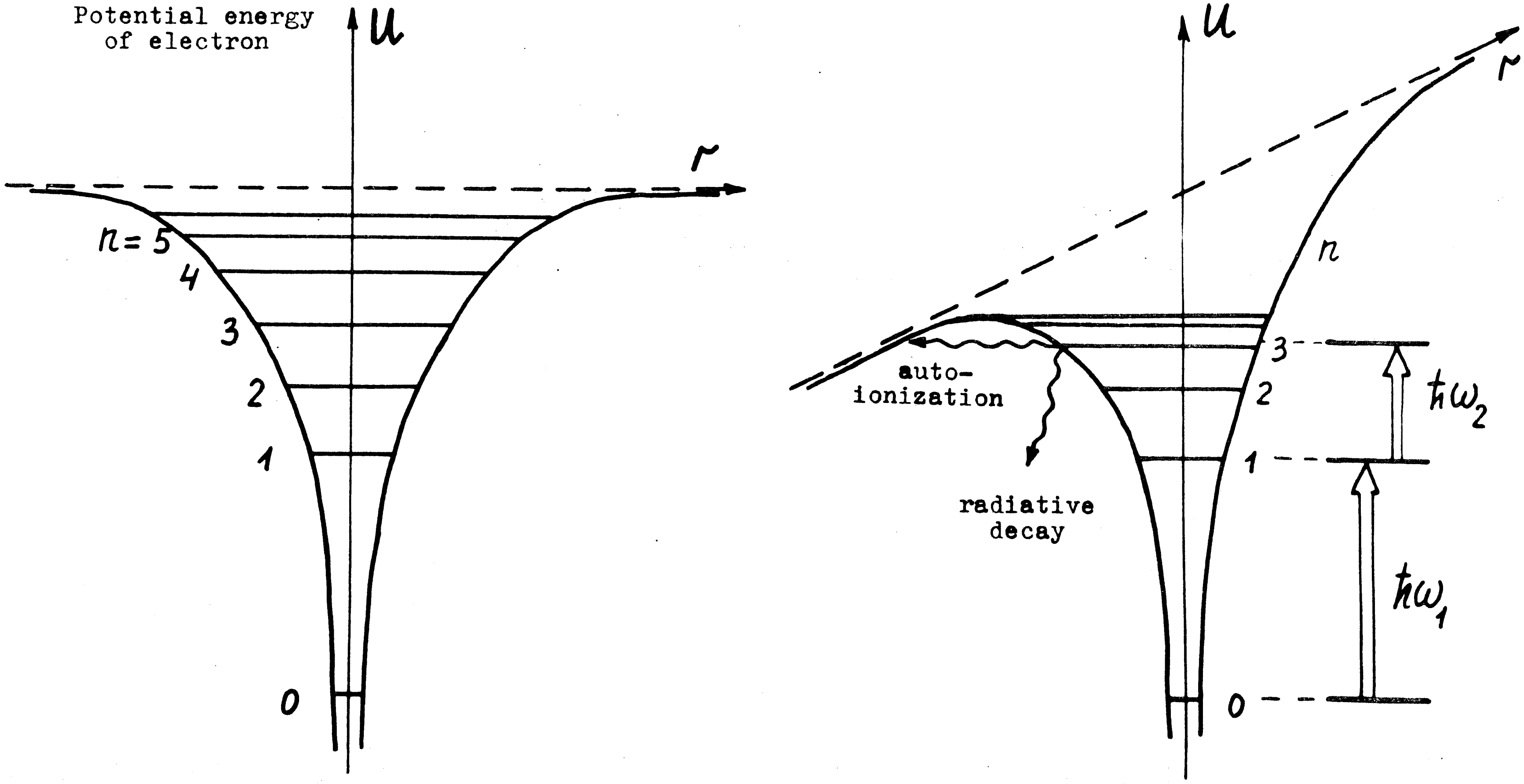
XBL 763-843

Fig. 13. The geometry of a setup for isotope separation through selective atomic photoionization in a sheet atomic beam.



XBL 763-844

Fig. 14. The spectrum of photoionization of uranium atoms from a state, excited by laser radiation at $\lambda_1 = 4266.324$ Å, produced by the use of a tunable dye laser (from /83/).

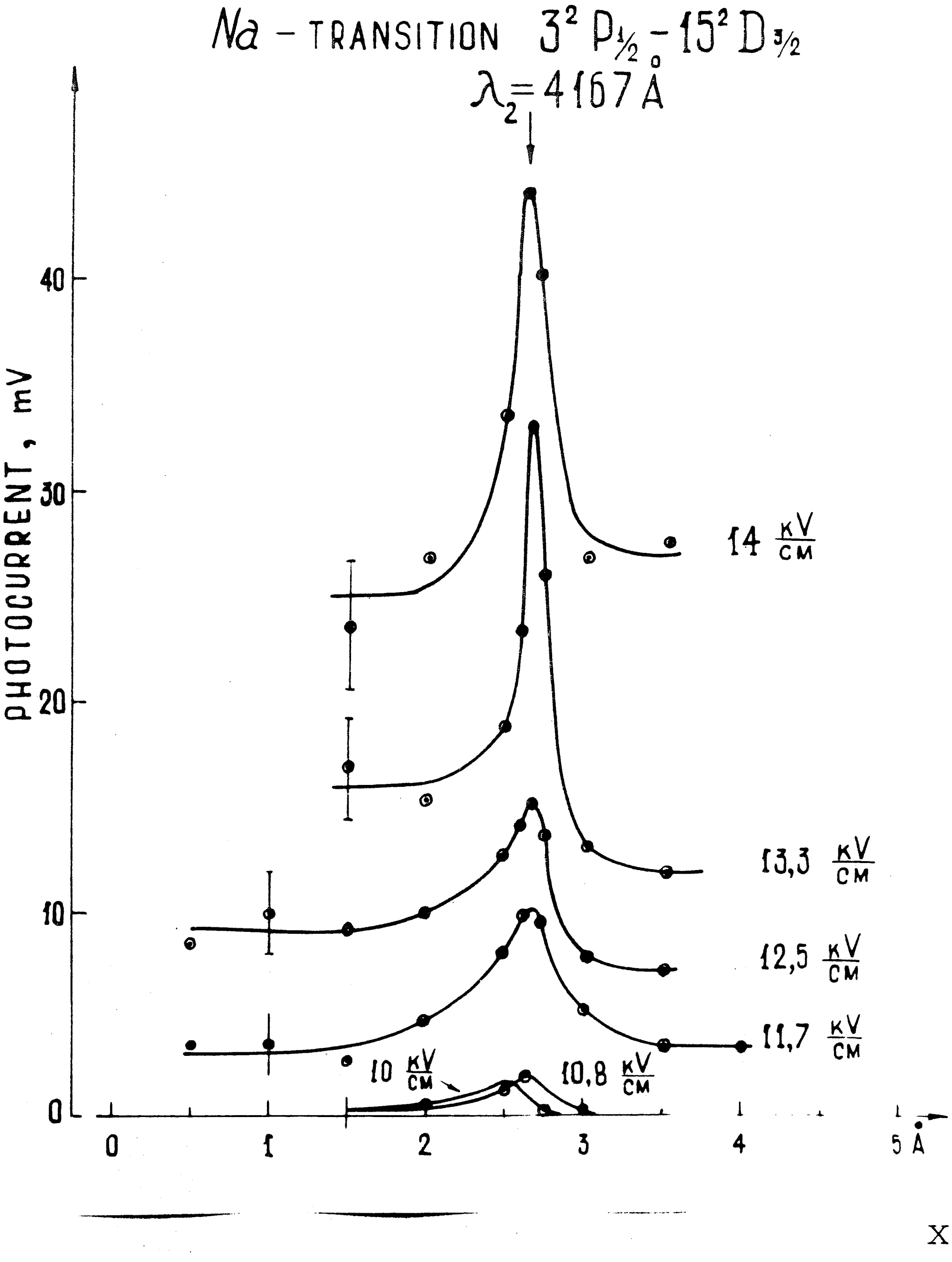


without electric field

under electric field

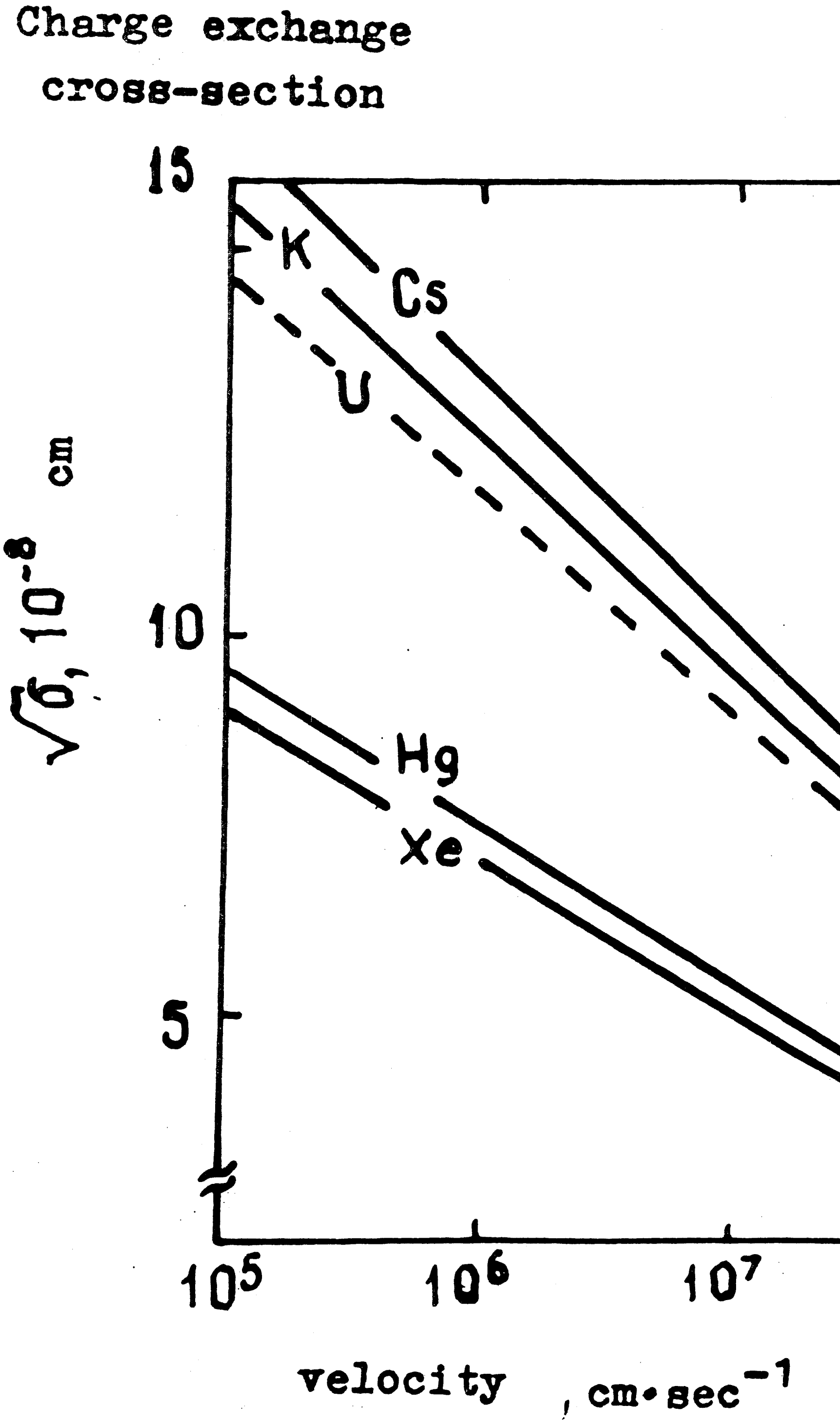
XBL 763-845

Fig. 15. Autoionization of high-excitation atomic states by external electric field; a) scheme of optical electron levels; b) potential rearrangement in the external electric field and formation of autoionization levels.



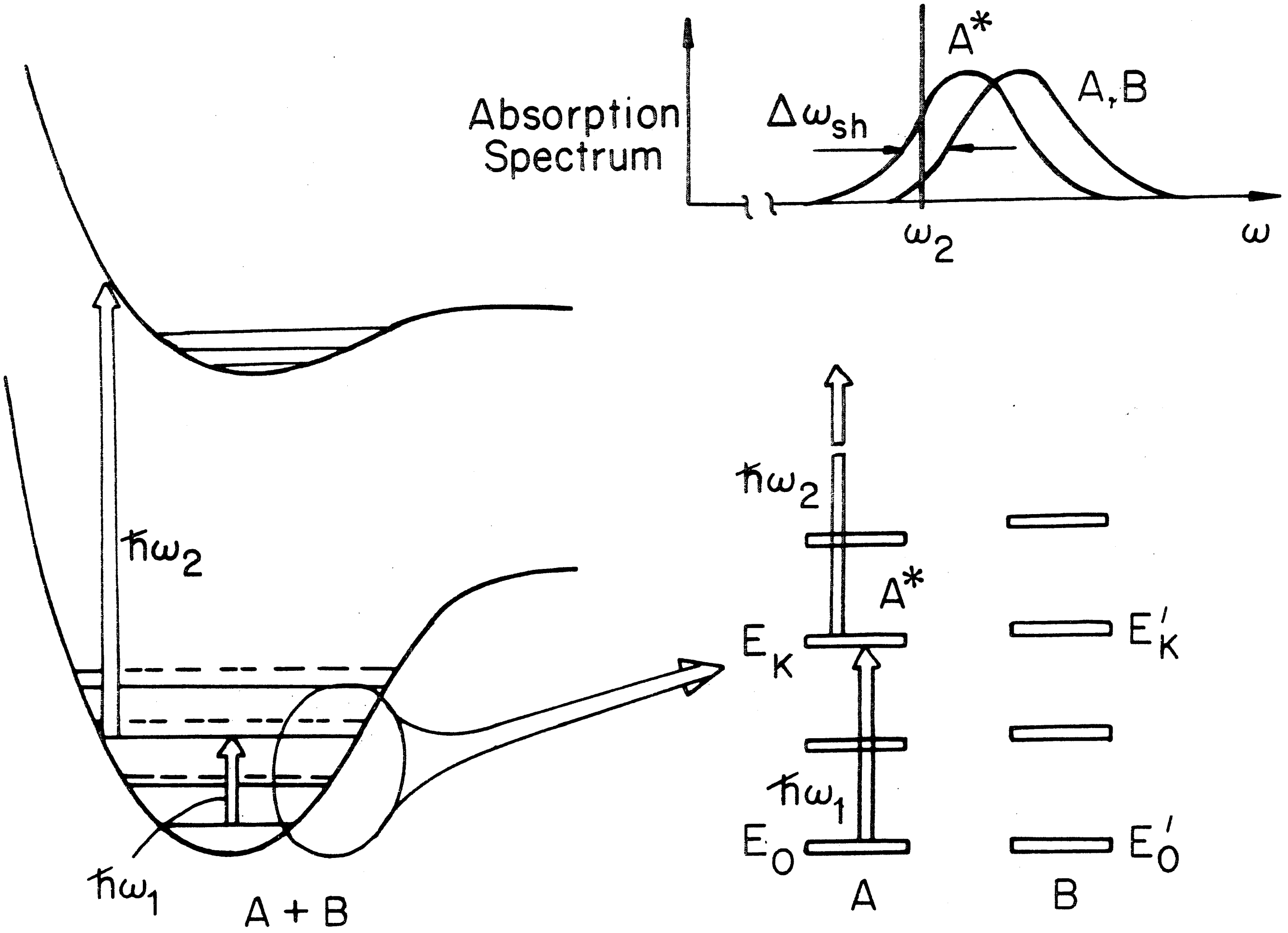
XBL 763-846

Fig. 16. The dependence of the signal of Na atom two-step photoionization through the autoionization state 15d induced by electric field on the wavelength of the second-step laser for varied values of electric field strength (from /87/).



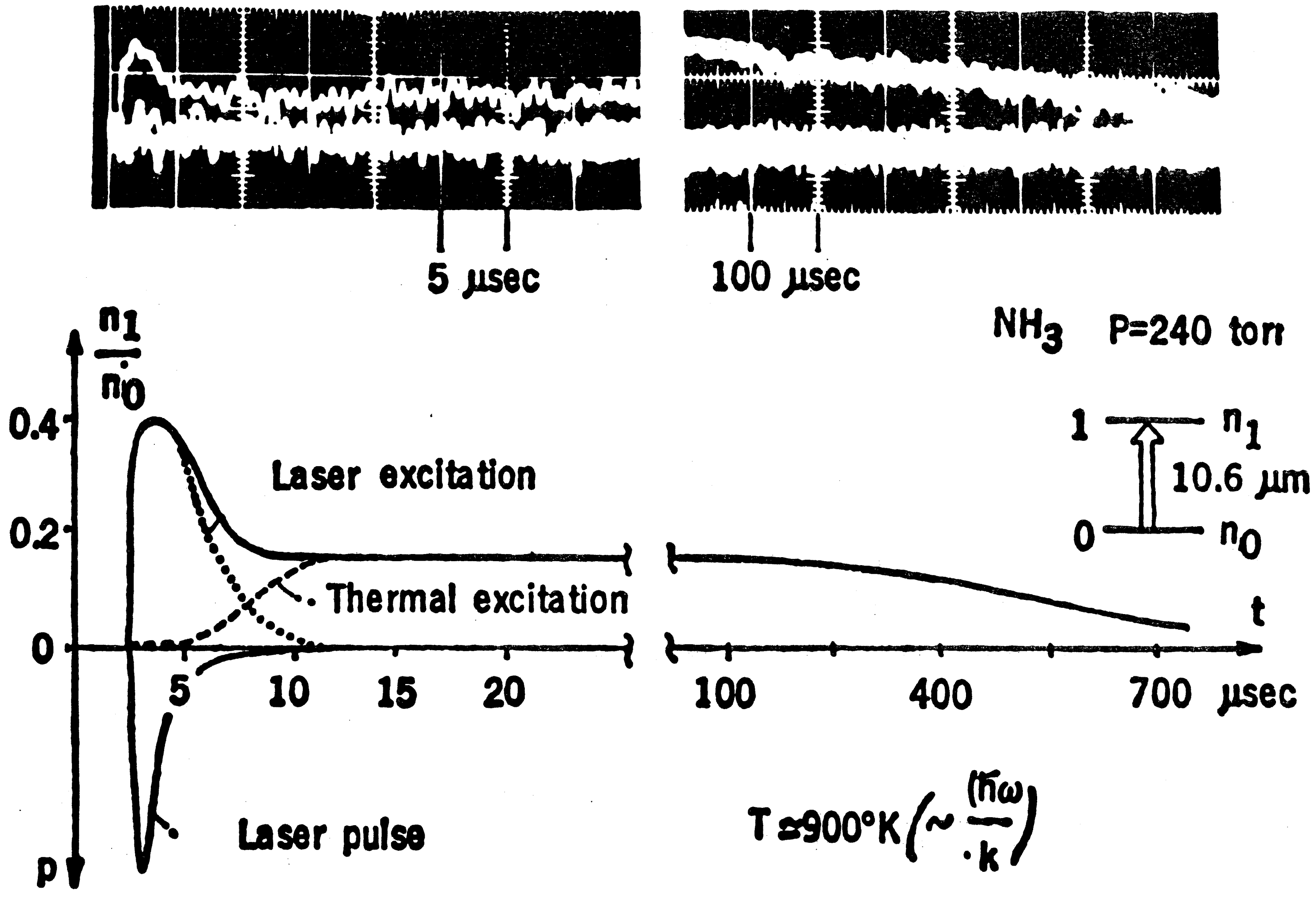
XBL 763-847

Fig. 17. The dependence of charge transfer cross-section on velocity for different ions.



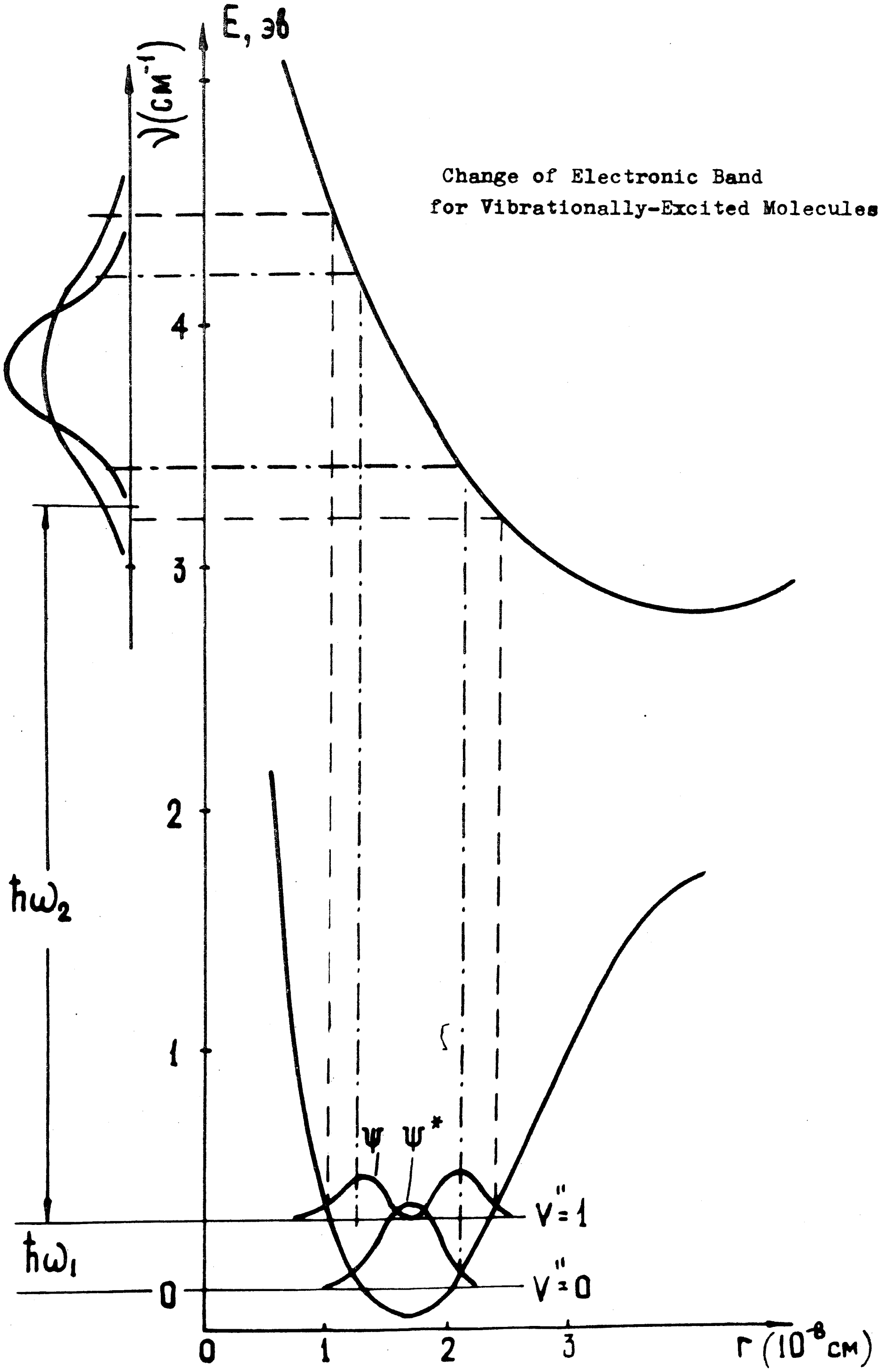
XBL 763-848

Fig. 18. Principal schemes for the process of selective two-step photodissociation of A molecules mixed with B molecules through the intermediate vibrational state $\mathcal{V}=2$. The diagram (at top) shows schematically the red shift of photodissociation boundary for vibration-excited A* molecules and the selection of the radiation frequency w_2.



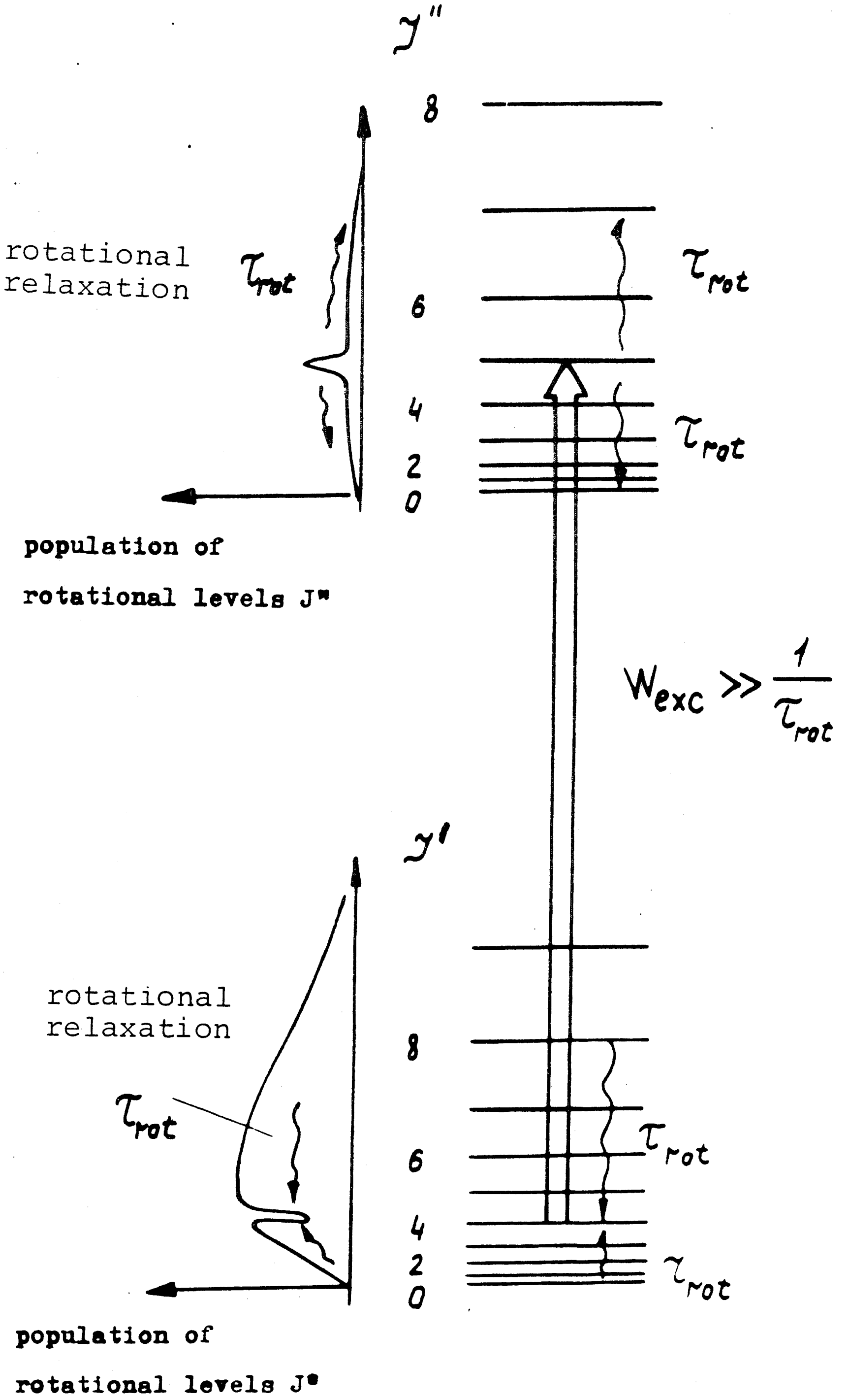
XBL 763-849

Fig. 19. The time dependence of population of the first ($\mathcal{V}=1$) vibrational state of NH_3 molecules under a CO_2 laser pulse (from /35,91/).



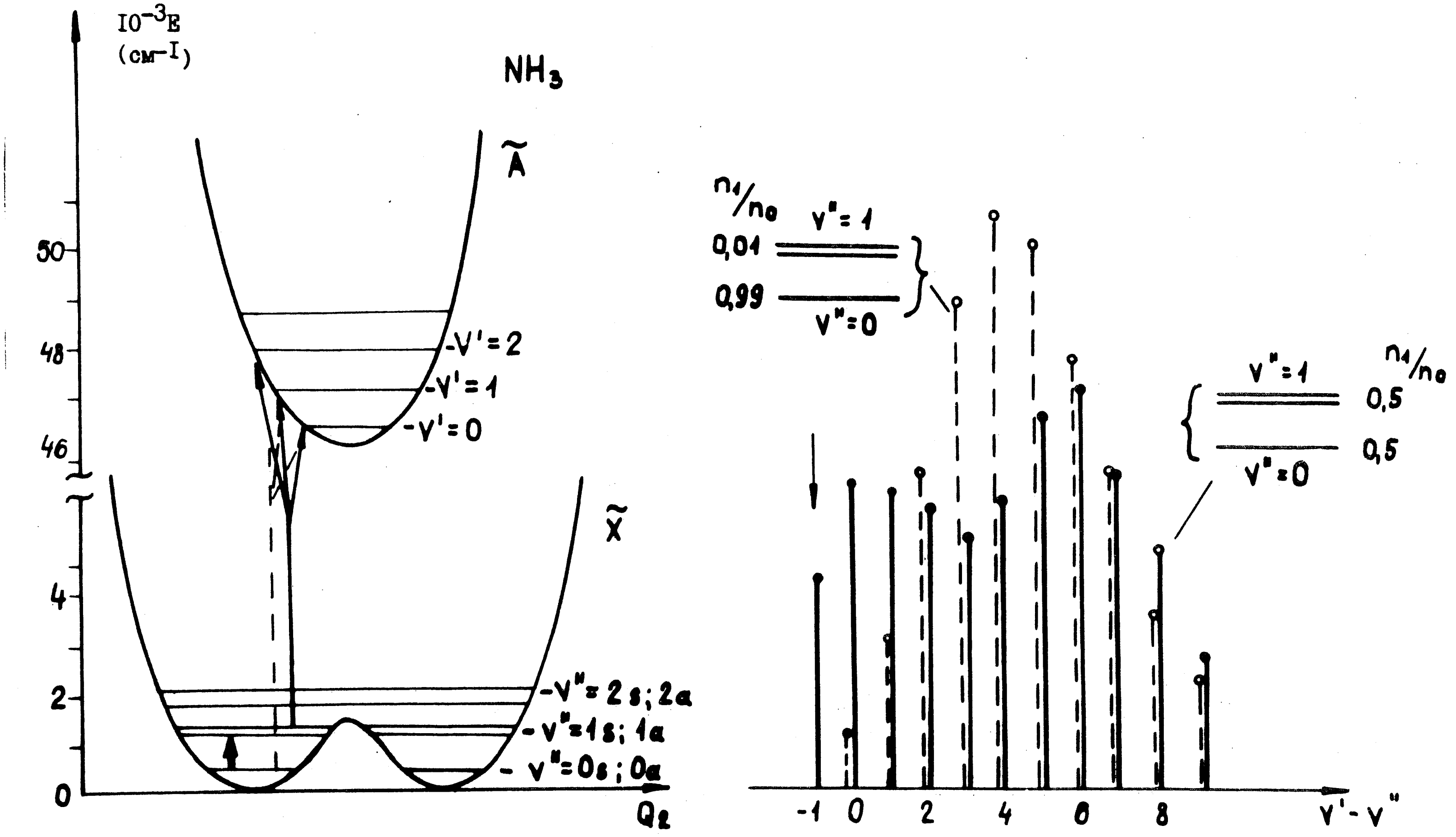
XBL 763-850

Fig. 20. The difference between the spectra of photoabsorption from the ground and excited vibrational states of a diatomic molecule.



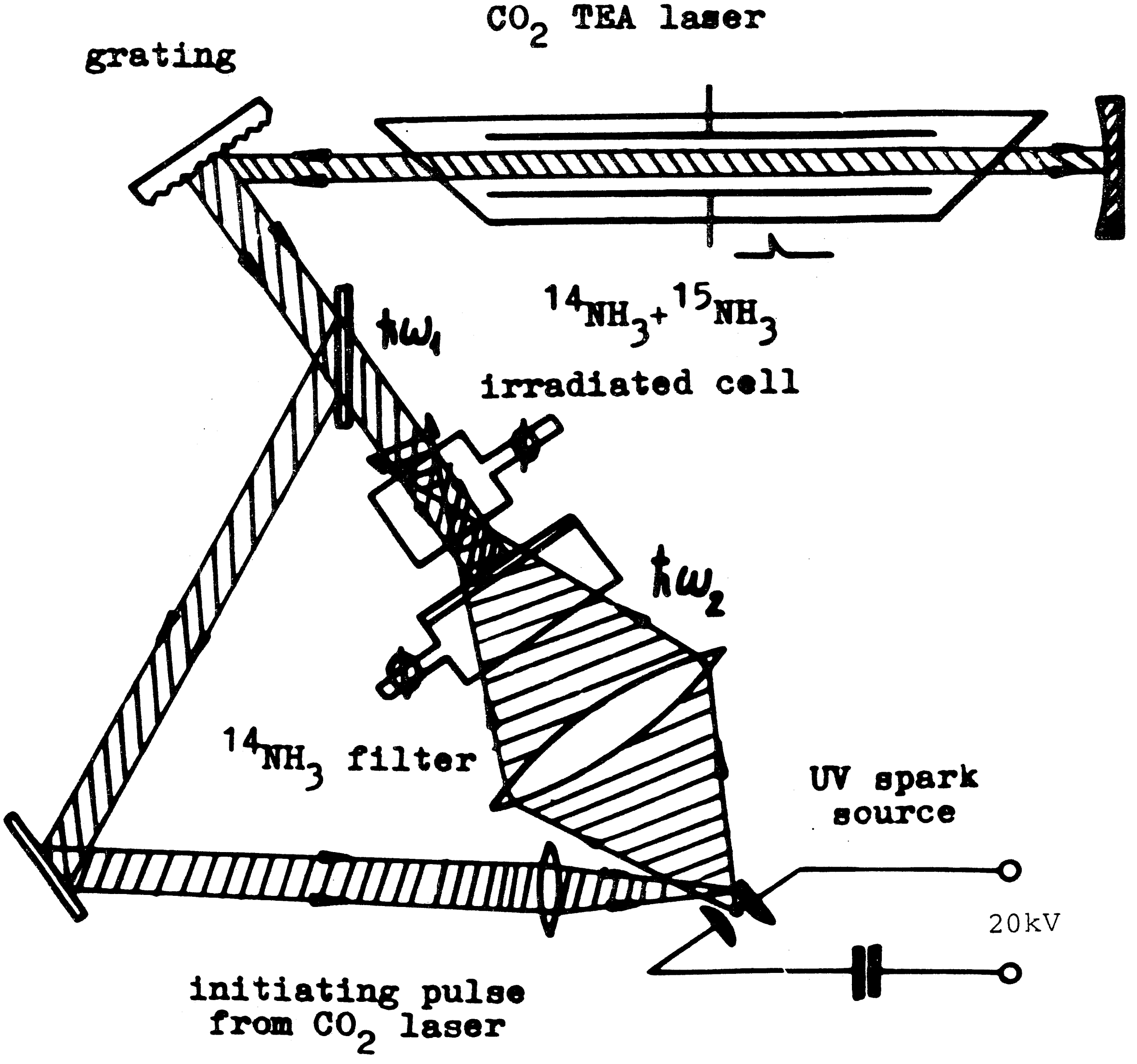
XBL 763-851

Fig. 21. **Explanations for the "bottle neck" effect when molecular vibrations are excited by monochromatic laser radiation.**



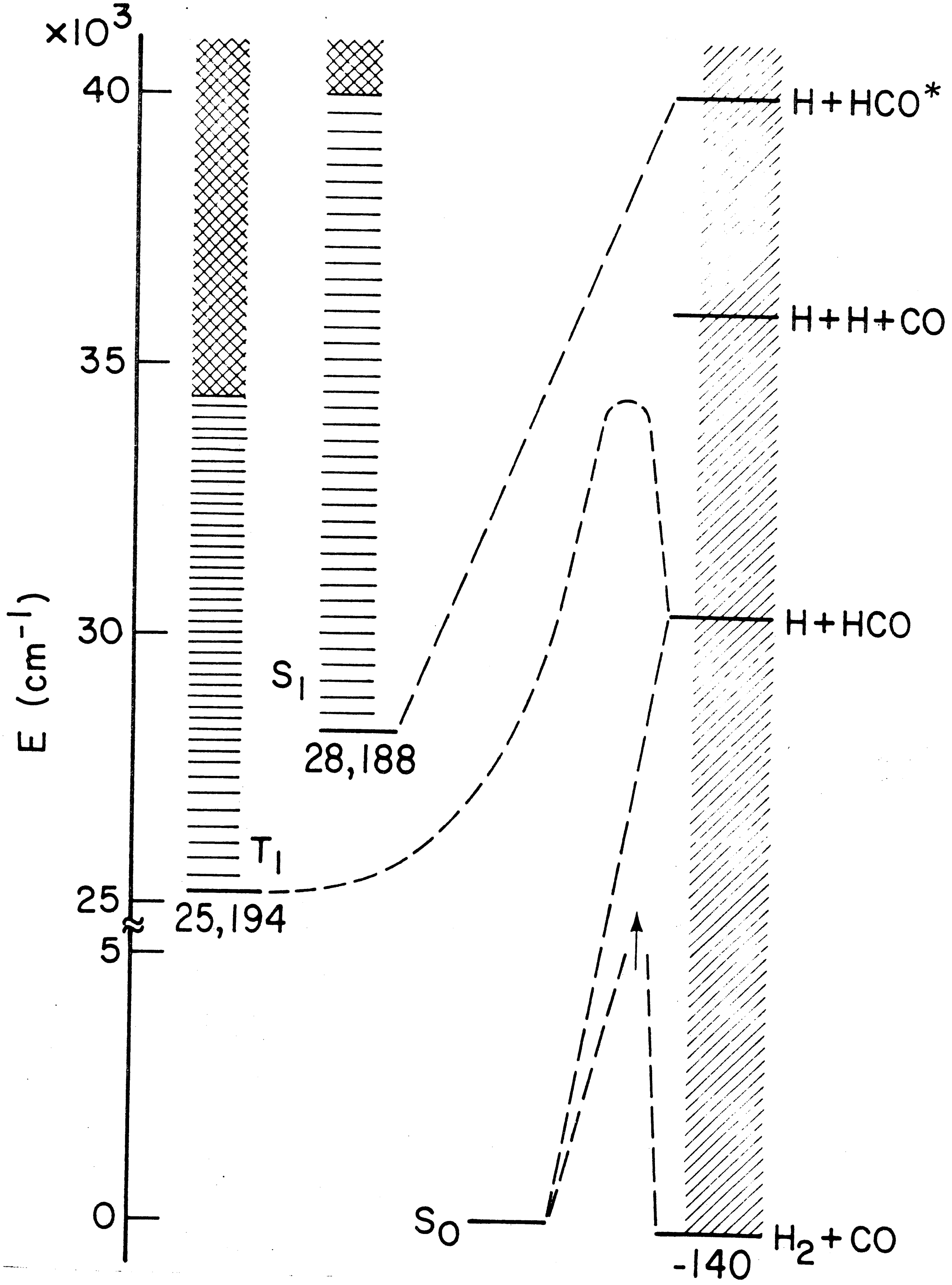
XBL 763-852

Fig. 22. The transition scheme of the ground electronic state of NH$_3$ molecules from vibrational states (v''=0,1) to excited electron-vibrational states (at left) and spectral lines (at right) caused by them (from /57/).



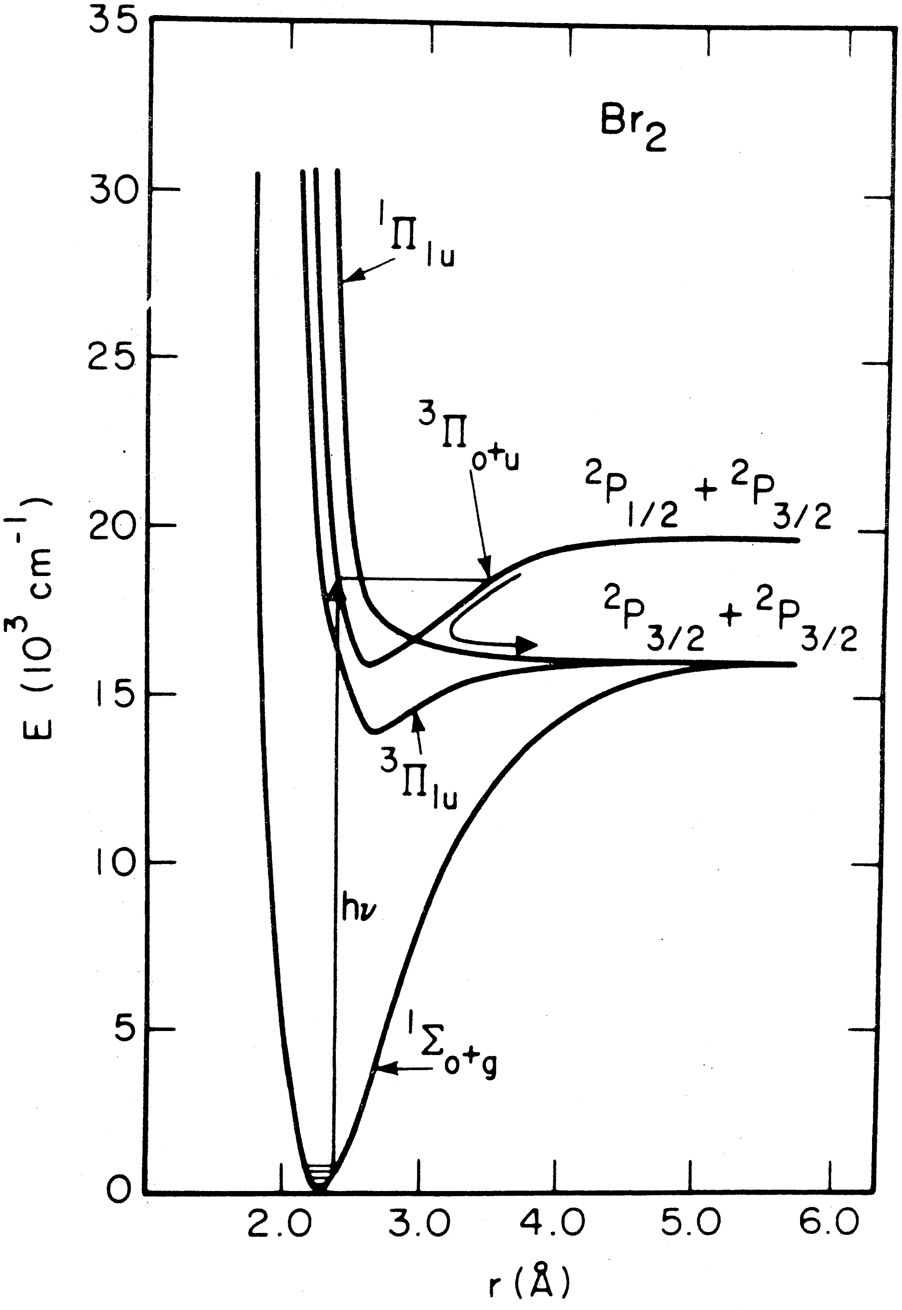
XBL 763-853

Fig. 23. The scheme of an experimental setup for nitrogen isotope separation by the method of two-step photodissociation of NH_3 molecules (from /26/).



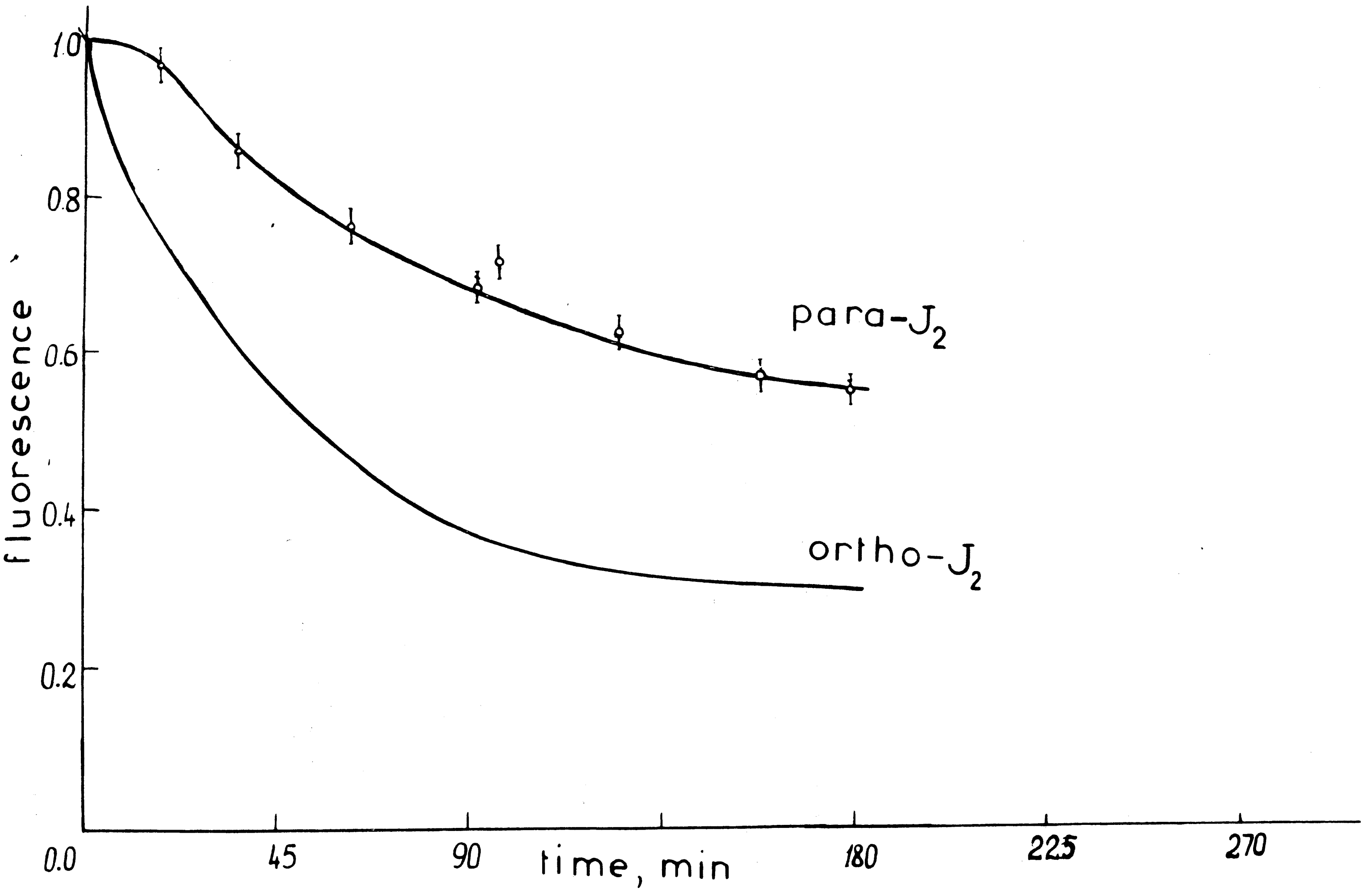
XBL 763-854

Fig. 24. Nonradiative predissociations of transition of H_2CO molecules from the first excited states (from /115/).



XBL 763-855

Fig. 25. The excitation and predissociation schemes of Br$_2$ molecules (from /119/).



XBL 763-856

Fig. 26. The kinetics of selective photopredissociation of ortho-I_2 molecules in the natural mixture with para - I_2 under agron laser radiation at 5145 Å (from /124/).

Laser isotope separation

Part II *)

V.S.Letokhov, C.B.Moore.

6. Molecular dissociation in a strong IR field

All the above-discussed schemes of laser isotope separation are based on excitation of electronic states of atoms and molecules by laser radiation in the visible or UV ranges of the spectrum. This method is based on the effect /1,2/ of selective collisionless molecular dissociation in the field of a powerful IR radiation pulse the frequency of which coincides with that of the molecular vibrational band. The discovery of this effect was preceded by works /3-6/ in which the interaction of a powerful IR pulse with molecular gases was investigated.

In work /3/ it is shown that, when focusing a powerful pulse of a CO_2 TEA - laser onto a molecular gas the vibrational absorption band of which coincides with the laser line, there appears visible luminescence if the field power in focus is below the threshold of optical breakdown (usually 10^8 - 10^9 W/cm^2). The intensity of luminescence is 2-4 orders lower than that of the spark which arises during an optical breakdown, and there are radical lines in the spectrum of visible luminescence. Similar results have been

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*) The first part of the review is published in the previous issue.

obtained in work /4/ on C_2F_3Cl molecules. These works have stimulated more detailed research into the mechanisms of molecular dissociation and visible luminescence under a strong IR field. The first studies on the kinetics of visible molecular luminescence under CO_2 laser pulses have shown /5/ that visible luminescence arises very quickly, with the delay time τ_d with respect to the leading edge of CO_2 laser pulse being shorter than 30 nsec, that is much shorter than the time of V-T relaxation and V-V vibrational exchange. Therefore, as noted in works /4,5/, this effect can not be associated with either thermal gas heating or collisional excitation of molecules in the process of exchange.

Fig.1 shows a typical experimental scheme to study the kinetics of visible luminescence by the action of a short CO_2 laser pulse.The beam of CO_2 TEA-laser is focussed onto a molecular gas cell. Luminescence is observed through a side window. Luminescence signals from a photomultiplier and the laser signal from a IR "photon-drag" detector are observed simultaneously. Fig. 1 shows also BCl_3 luminescence pulses from different regions: focal (A) and off-focal (B). In the region of laser pulse focus two kinetic stages of luminescence are observable /6/, instantaneous and retarded At low pressures of BCl_3 (2-3 Torr) these stages are quite distinct. As the pressure is increased, the retarding stage appears to approximate the instantaneous one and they can not be distinguished any longer. In the off-focal region, that is the region of strong field, only the retarded luminescence stage is observed. Instantaneous luminescence can be observed down to very low pressures of about 0.03 Torr with its pulses of up to 40 nsec long and has no observable delay with respect to the laser pulse. Retarded luminescence is collisional in nature. This is confirmed by the relation $p\tau$ = const (for BCl_3 const = =2.3 μsec/Torr), where P is the gas pressure in the cell, τ is the delay time of retarding luminescence maximum with respect to the beginning of laser pulse. Retarding luminescence may be explained by dissociation of highly excited molecules as they reach the dissociation limit owing to V - V exchange during collisions after the laser pulse is over. Detailed studies on the kinetics of molecular luminescence have been carried out in works /6,7/ on BCl_3 and in /8/ on SiF_4 molecules.

The essential features of this "instantaneous" luminescence are that it is observed at an intensity of the resonant IR field of about 10^9 W/cm^2 and that it occurs simultaneously with the laser pulse even though the time between molecular collisions τ_{coll} is much longer than the laser pulse. At a pressure of 0.03 Torr the time between molecular collisions in BCl_3 τ_{coll} = 1.3 μsec. Therefore the probability of one collision during a laser pulse τ_L =40 nsec equals 0.03, of two collisions - $(0.03)^2=10^{-3}$, etc. So, the collisional mechanism of molecular excitation up to the limit of dissociation during a laser pulse is completely excluded, and the appearance of an "instantaneous" luminescence stage is related to dissociation of an isolated molecule under only the action of a strong IR field due to multiphoton absorption.

The effect of collisionless molecular dissociation in a strong IR field has opened one more possibility for photophysical action on molecules which may be isotopically selective provided the isotope shift is well resolved in the IR spectrum. The first experiments on isotope separation by this method were run in work /1/ on BCl_3 molecules which had two nonoverlapping absorption bands of isotopic molecules $^{10}BCl_3$ and $^{11}BCl_3$. In these experiments the products of BCl_3 dissociation reacted with oxygen , with the result that the electron-excited radical BO was formed. The BO radical has an intense system of lines, known as a α-band, with well-resolved bands for ^{10}BO and ^{11}BO. The isotope shift in the luminescence spectrum of BO is about 30 Å, that facilitates the isotopic analysis of reaction products.

The experiment in work /1/ was conducted thus: a CO_2 laser was tuned to the absorption band of ν_3 mode of either $^{10}BCl_3$ or $^{11}BCl_3$ molecules, and the line intensity for ^{10}BO and ^{11}BO was studied. The experiment employed the natural isotope mixture (^{10}B : ^{11}B = 1 :4.32). The section of BO luminescence spectrum at the transition (0.2) of the band $^2\Pi \rightarrow {}^2\Sigma$ was studied. The recording system made it possible to resolve time intervals 150 nsec long within different sections of BO luminescence pulse. Because of this it was possible to study the selectivity of BO formation at the instants corresponding to both instantaneous and retarding luminescence stages in pure BCl_3. Fig.2.presents the sections of BO luminescence spectrum at a pulse maximum (it corresponds to the retarding stage in pure BCl_3) during excitation of $^{10}BCl_3$ and $^{11}BCl_3$ (the pressure of BCl_3 mixed with N_2+O_2 being 4 Torr, O_2 - 4 Torr, N_2 - 16 Torr). One can clearly see that when tuning to the absorption band of $^{10}BCl_3$ the ^{10}BO radical is formed mainly, and ^{11}BO when tuning to $^{11}BCl_3$. With further increase in the delay time of the time interval under observation with respect to the pulse laser up to 1.2 μ sec, that is, to the end of BO luminescence pulse the spectrum did not materially change. So, the process of BO formation during the both stages is selective. On the basis of the data on BO visible luminescence spectrum the enrichment coefficient is evaluated, which equals (R.V.Ambartzumian et al /1,7/):

$$K(^{10}B/^{11}B) = \frac{[^{10}BO]\,[^{11}BCl_3]}{[^{11}BO]\,[^{10}BCl_3]} \simeq 10 ,$$

when $^{10}BCl_3$ molecules are excited by the R(24) line of CO_2 laser. The experiments, in which BO luminescence is observed in the off-focal region, have also provided support for the presence of isotopically-selective chemical reactions /7/.

Important experiments were run in work /9/ that has displayed macroscopic separation of ^{10}B and ^{11}B isotopes. In these experiments the relative content of remaining $^{10}BCl_3$ and $^{11}BCl_3$ molecules was measured using the IR absorption spectrum of the residual gas mixture. The results of such experiments are given in Fig.3. The last (on the left) IR spectrum corresponds to unirradiated natural mixture of $^{10}BCl_3$ and $^{11}BCl_3$, while the other spectra are given for absorption of the mixture irradiated by a CO_2 laser tuned to the absorption band of $^{10}BCl_3$ or $^{11}BCl_3$. O_2,C_2D_2,HBr and other molecules were used as acceptors. In the case of O_2- acceptor the resultant BO radicals reacted and formed the stable product B_2O_3 which was deposited on the walls as a white thin coating. The typical enrichment coefficient at low pressures was K $(^{10}B/_{^{11}B}) \simeq 8$, but its value decreased sharply with increasing pressure of BCl_3.

The experiments on sulphur isotope separation (R.V.Ambartzumian et al /2/) based on selective chemically-irreversible dissociation of one of the SF_6 isotopic molecules in a strong IR field have given more conclusive evidence of the efficiency and simplicity of this isotope separation method. In these experiments the reaction cell was filled with SF_6 of natural isotopic composition, and the CO_2 laser was tuned to a frequency corresponding to the absorption maximum of either $^{32}SF_6$ (95%) or $^{34}SF_6$ (4,2%). The natural mixture contained also $^{33}SF_6$ (0,75%) and $^{36}SF_6$ (0.017%) molecules. In contrast to BCl_3, the process of SF_6 dissociation in a strong IR field is irreversible, and there is no need to add radical acceptors. In some cases H_2, HBr and NO were used as acceptors. For all these acceptors, as well as without them, the results obtained were qualitatively the same. When the CO_2 laser frequency was tuned to the maximum of $^{32}SF_6$ absorption band at 947 cm^{-1}

(the line P(16) of CO_2 laser) and the cell (SF_6 - 0,18 Torr, H_2 - 2 Torr) irradiated by $2 \cdot 10^3$ pulses, almost all $^{32}SF_6$ molecules disappeared from the mixture owing to selective dissociation. The mass spectrum of SF_5^+ consisted mainly of lines corresponding to $^{32}SF_6$ and $^{34}SF_6$ molecules (Fig.4). The coefficient of absorption by ^{34}S isotope with respect to ^{32}S was evaluated (about 2800) from the ratio of mass line amplitudes before and after irradiation. In analogous experiments the coefficient of mixture absorption by ^{36}S with respect to ^{32}S was $K(36/32) \simeq 1200$.

For physical isotope separation the residual gas was frozen out of the cell under irradiation. The results of enrichment measurements by IR and mass spectra of residual gas were coincident.

In works /10,11/ the dependence of the enrichment coefficient on laser radiation intensity, gas pressure and pulse number was investigated in detail. The results of studies on the relation between K(34/32) and radiation intensity are listed in Fig.5. The measurements were taken in a focussed laser beam when the radiation power was nonuniform in volume. For a better understanding of power in volume the top scale presents power values in the focal region and the lower one gives the value of average power density defined as $I_{aver} = \frac{PL}{V}$, where P is incident power, V in the volume illuminated in the cell, L is the cell length. It is clearly seen that the selectivity of enrichment process is very responsive to the variation of laser radiation intensity.

Fig.6 illustrates the dependence of K(34/32) in the residual mixture on the initial pressure of SF_6 in the cell at a varied number of radiation pulses measured in work /10/. The value of enrichment coefficient sharply decreases with P pressure as exp$(1/p)$ and reaches its peak at SF_6 pressures below 0,5 Torr. With increasing SF_6 pressure the coefficient K tends to unity, that is, there is no enrichment. A decrease in the enrichment coefficient with increase in the pressure of SF_6 may be caused by increasing contribution of nonselective dissociation of SF_6 due to thermal gas heating resulted by vibrational-translational relaxation of those excited molecules which do not reach the dissociation limit. At low pressures this effect is absent, since the time of molecular wall diffusion becomes much shorter than that of V-T relaxation and the molecules become deactivated without heating the gas.

In Fig.6 one can see also the dependence of the enrichment coefficient on the number of radiation pulses. It should be kept in mind that this dependence does not characterize the selectivity of an elementary process of molecular dissociation because it is governed by the portion of undissociated molecules in the whole volume. Qualitative analysis in the simplest model of dissociation of a two-component isotopic molecular mixture was carried out in work /10/. Let the initial concentrations of molecules be N_{ao} and N_{bo}, and IR radiation pulses are in resonance with the N_{ao} molecules which contain the isotope "a". Denote the dissociation rate of "a" molecules by

d_a and that of "b" by d_b. The value d_a (d_b) is determined by volume-averaged probability of irreversible dissociation of one molecule "a" under the action of one pulse and by the number of pulses per unit time. Since the molecule "a" is in better resonance with the field, $d_a > d_b$, and the molecular dissociation selectivity is determined evidently by the relation $S = d_a/d_b$ ($S \gg 1$ corresponds to high selectivity). The concentrations of "a" and "b" molecules decrease exponentially with time (or the number of pulses):

$$N_a = N_{ao} \exp(-d_a t) \; ; \; N_b = N_{bo} \exp(-d_b t) \qquad (6.1)$$

It is assumed that, as the source molecules burn up and the chemical composition and pressure of the gas mixture change, the values of dissociation rate remain constant. At low gas pressures, which are of most interest for high enrichment, this is quite a tolerable first approximation since the process of dissociation depends mainly on IR field. In this case the coefficient of residual gas enrichment with an isotope, according to (6.1), equals:

$$K_{res}(b/a) = \left(\frac{N_b}{N_a}\right) \Big/ \left(\frac{N_{bo}}{N_{ao}}\right) = \exp(d_a - d_b)t = \exp\left(\frac{S-1}{S} d_a t\right) \qquad (6.2)$$

The total pressure of residual gas $N = N_a + N_b$ varies thus:

$$\frac{N}{N_0} = \delta_a \exp(-d_a t) + \delta_b \exp(-d_b t), \qquad (6.3)$$

where $N_0 = N_{ao} + N_{bo}$, $\delta_a = \frac{N_{ao}}{N_0}$, $\delta_b = \frac{N_{bo}}{N_0}$ denote the relative content of isotopic molecules in the source mixture.

The enrichment coefficient of product molecules is determined by the relation:

$$K_{prod} = \frac{N_{a0} - N_a}{N_{b0} - N_b} \Big/ \frac{N_{a0}}{N_{b0}} = \frac{1 - \exp(-d_a t)}{1 - \exp(-d_b t)} \qquad (6.4)$$

With the degree of decomposition of source mixture small ($d_a t$, $d_b t \ll 1$), we have:

$$K_{prod}\,(a/b) = \frac{d_a}{d_b} = S \qquad (6.5)$$

that is, the enrichment of resulting molecules depends on the degree of dissociation selectivity of "a" molecules.

Relations (6.3) - (6.5) show that at exponentially deep "burning" of source molecules "a" and "b" the small portion of remaining molecules can be enriched with the isotope "b" as much as one wants. Fig.7 illustrates the time (or pulse number) variation fo enrichment coefficients of remaining and resulting molecules for three different values of dissociation selectivity factor (S = 1.1 small, S=2 moderate and S=10 high selectivity).

In the experiments described in works /2,10/ the coefficients of enrichment by sulphur isotopes K(34/32) and K (36/32) were $> 10^3$ under sufficiently deep molecular burning (the pressure of residual SF_6 gas was below 1% of the initial one). Under deep molecular burning the enrichment coefficient of residual gas is not equal, of course, to the coefficient of molecular dissociation selectivity S, and the latter must be evaluated by the use of (6.3) and (6.4), that is, the enrichment coefficient K_{resid} (b/a) and variation of residual gas pressure must be measured simultaneously.

Fig.8 presents the experimental values of enrichment coefficients for residual SF_6 gas and resulting molecules at a comparatively high pressure of SF_6 (16 Torr) when the enrichment magnitude is far from maximum possible values. When approaching to the regime of deep molecular burning one can clearly observe an increase in K_{resid} (34/32) and the beginning of decrease in K_{prod} (32/34). The value of K_{prod} (32/34) at the beginning of irradiation produces at once the value for the coefficient of $^{32}SF_6$ dissociation selectivity (at SF_6 pressure of 1.6 Torr $S=3.5$). As the pressure is decreased down to 0.2 Torr, the dissociation selectivity increases greatly and may be as high as $S \gg 10$.

Maximum possible isotopic selectivity in molecular dissociation is a problem of principal interest for isotope separation. Some idea about this is given by the dependence of K(33/32) and K(34/32) on frequency detuning of $^{33}SF_6$ and $^{34}SF_6$ absorption bands with respect to the band of the $^{32}SF_6$ molecule under dissociation. This dependence given in Fig.9 has been obtained in work /10/. The enrichment coefficient increases exponentially with isotope shift. During deep burning, when K_{resid} is related to the dissociation selectivity S by (6.3), this corresponds at least to linear increase of S as the isotope shift between the centres of molecular absorption bands increases.

In the regime of deep burning marked enrichment may be attained even at very small dissociation selectivity. This is confirmed by the successful experiments /12/ on

^{187}Os and ^{192}Os isotope separation through dissociation of OsO_4 molecules by CO_2 laser pulses. The value of isotope shift in the vibrational bands of these isotopes is 1.3 cm^{-1}, that is much smaller than the absorption bandwidth (the half-width of the Q-branch of ν_3 mode for OsO_4 is 3-4 cm^{-1}). The enrichment coefficients obtained are about 12-15%. It is noted in work /12/ that such low enrichment coefficients are due to a low power level of the CO_2 laser at the P(2) and R(2) lines (70 MW/cm^2 in the lens focus), for the enrichment coefficient increases exponentially with intensity (Fig.5).

Successful experiments on isotope separation in macroscopic amounts (in the first experiments /2/ the rate of twenty-fold enrichment was 10^{-4} gr/min using a simple TEA CO_2 laser with its pulse power of 2 J and frequency of 1.5 Hz) drew the attention of many laboratories to this method. In particular, experiments on sulphur isotope separation were reproduced in work /13/. Work /14/ confirms results of works /1,9/ on boron isotope separation and also successful experiments on isotope separation of chlorine (25% - enrichment) and carbon (62% - enrichment) through dissociation of CF_2Cl_2 molecules, as well as silicon (16% -enrichment) through dissociation of SiF_4 molecules. It is evident that the method can be applied to separation of rather a great number of isotopes using accessible and inexpensive IR radiation of molecular gas lasers with high efficiency.

The potentialities and practical significance of the separation method considered have grown much more since the discovery /16/ of the effect of selective molecular dissociation when acting with a strong IR field on very weak molecular overtones (on SF_6 and CCl_4 molecules). For example, when the compound vibrations $\nu_2 + \nu_6$ and $\nu_2 + \nu_3 - \nu_5$ of the SF_6 molecule (the fundamental vibration ν_3) are acted upon, the molecule can be dissociated, and the dissociation rate drops as the square root of compound band intensity, that is, not too quickly. Analogous experiments have been conducted on CCl_4 molecules. It has been revealed /17/ that some compound vibrations do not contribute to dissociation, on other molecules isotopically-selective dissociation has been observed with the coefficient of enrichment of resulting products with the isotope ^{13}C being between 7 and 10. These results are of interest in understanding the mechanism of multiphoton absorption by vibrations of polyatomic molecules as well as in widening the scope of the isotope separation method for many other molecules whose fundamental vibrational bands of absorption coincide with radiation frequencies of available high-power IR lasers. Thus, the method of instantaneous selective molecular dissociation in a strong IR field due to multiphoton absorption seems to be very promising and efficient for isotope separation by the use of laser radiation.

Since molecular dissociation in a strong IR field needs a total radiation energy of 10-20 eV only, isotope separation by this method may appear to be useful with regard to energy even for large-scale processes of enrichment of such rare elements as deuterium. The dissociation of C_2H_4 molecules in a strong field of CO_2 laser makes it possible to use the method for molecules existing in the nature in large amounts (natural gas).

7. ELECTRONIC PHOTOCHEMISTRY

The chemical reactions of electronically excited atoms and molecules have been an active subject of research for many years. The first photochemical isotope separation was attempted by Hartley et al/19/ in 1922. Since the energies of electronic excitation are on the order of a chemical bond it is natural to expect that molecular excited states will often be more reactive than ground states. Recently the application of orbital correlation diagrams/20,21/has considerably improved our understanding of photochemical reactions and our ability to predict the relative reactivity of ground and excited states.

Selective excitation of electronic states is possible for most atoms and diatomic molecules. Herzberg /22/ lists spectra of polyatomic molecules with as many as twelve atoms. Although most stable polyatomic molecules do not have transitions with well-resolved rotational structure and isotope shifts in the visible and near ultraviolet there are many which do. There are thus many elements for which isotope separation by electronic photochemistry may be possible.

For successful isotope separation one must find an absorbing atom or molecule and a coreactant which do not react either in the gas phase or on the container walls under the ambient conditions. The excited state must react more rapidly than it loses its excitation by radiation, by predissociation, by energy transfer to molecules containing the undesired isotopes or by quenching. Collisions of the excited molecule with the coreactant should result in chemical reaction more often than in physical quenching. The absolute reaction rate constant should be large enough so that collisions with the coreactant are the primary route of excitation loss at pressures low enough so that pressure broadening does not degrade the excitation selectivity. Finally, the reaction products must be stable and may not undergo further reactions with the unexcited molecules. If free radicals or other unstable molecules are produced in the primary reaction step, they must be scavenged chemically before any isotope scrambling reactions occur. It is unfortunate that most of the photochemistry of small molecules involves the formation and subsequent reactions of free radicals /23/.

The photochemical isotope separation of Hg excited by the 253.7 nm resonance line has been successfully demonstrated with a variety of reagents. Pertel and Gunning /24/ were able to enrich ^{202}Hg from a 30% natural abundance to 85% in a mixture of Hg, H_2O and butadiene. The kinetics of the photochemical reactions of Hg are sufficiently complex that even the extensive work of Gunning and his collaborators /24-34/ does not give a complete mechanism. Even so, many important features of photochemical isotope separation are illustrated by this work. Several primary processes are possible in collisions between excited Hg and H_2O:

$$^{i}Hg^{*} + HOH \longrightarrow {}^{i}HgOH + H \qquad (7.1)$$

$$\longrightarrow {}^{i}HgH + OH \qquad (7.2)$$

$$\longrightarrow {}^{i}HgO + H_2 \qquad (7.3)$$

$$\longrightarrow {}^{i}Hg + OH + H \qquad (7.4)$$

$$\longrightarrow {}^{i}Hg + HOH \qquad (7.5)$$

Isotopic enrichment is possible only when ^{i}Hg is chemically bonded in this first step as in (7.1), (7.2) or (7.3). The quenching process (7.5) gives no chemistry at all. The mercury sensitized dissociation of H_2O (7.4) may well lead to stable product molecules containing Hg, but there will be no isotopic selectivity.

$$OH + {}^{n}Hg \longrightarrow {}^{n}HgOH \qquad (7.6)$$

$$\longrightarrow {}^{n}HgO + H \qquad (7.7)$$

HgOH itself is not stable but reacts further to the final product HgO. Isotopic scrambling could occur by

$$^{i}HgOH + {}^{n}Hg \longrightarrow {}^{i}Hg + {}^{n}HgOH\ . \qquad (7.8)$$

H and HgH may play roles in the production of the final product HgO. In pure Hg-H_2O mixtures enrichment factors less than 1.3 were found /24/. However, a separation factor of

13 was found under the best conditions in mixtures of Hg-H_2O-C_4H_6 /24/. From this observation it may be concluded that the primary process is (7.1) or (7.2) and that butadiene must react with H and OH and perhaps with HgOH or HgH in such a way as to terminate most of the isotope scrambling processes such as (7.6), (7.7) and (7.8). Reaction (7.3) must not occur to a major extent since its products would be stable without addition of butadiene.

Isotopic enrichment in diatomics has been carried out by Harteck and his coworkers using atomic resonance lamps for excitation. Excitation of NO with a Br lamp at 163 nm produced $^{14}N^{15}N$ enriched by as much as a factor of 4 /35/. Photolysis of CO with 206 nm light from an I lamp preferentially excites ^{13}CO and $C^{18}O$ about a factor of 30 more strongly than the abundant isotope. The spectroscopic selectivity was apparently degraded by about a factor of six due to energy transfer between CO molecules /36/.

Laser sources for photochemical isotope separation have several advantages over incoherent sources. The number of favorable chance overlaps between isotopic molecular absorption lines and atomic resonance lines is severely limited. The broad tunability and high ultimate resolution of dye lasers gives a free choice of absorptions in the visible and near ultraviolet and allows the highest possible selectivity. For molecular transitions, especially of relatively rare isotopes only a small fraction of the uncollimated light from an incoherent source will be absorbed in a photochemical reactor.

Two successful schemes of photochemical enrichment have been reported for the diatomic halogens. In work /37/ ortho-I_2 was excited with the 514.5 nm line of an Ar^+ laser. They found that in mixtures with 2-hexene the ortho-I_2 was reduced to about 5% as a result of a 1 hr irradiation with a 0.2 W laser. The kinetics were studied using the time dependence of fluorescence which was proportional to the density of ortho-I_2 molecules excited by the argon laser at 514.5 nm. The character of time variation of fluorescence is shown in Fig.10. The fluorescence signal decreases by e times throughout 5 min and then drops slowly over 60 min and becomes constant. The fluorescence signal which is proportional to the density of para-I_2 molecules and excited by a weak test laser beam at the wavelength of 501.7 nm does not change within the limits of measurement accuracy. Thus, as the reactor is irradiated by a laser, the excited ortho-I_2 molecules react with 2-hexene and para -I_2 remains unreacted. Halogenation of olefins (2-hexene) in gas phase follows the radical-chain mechanism /38/. The process of direct addition of an excited iodine molecule to the olefin X has been solved by excitation, however:

$$o\text{-}I_2^* + X \longrightarrow XI_2 \tag{7.9}$$

In this case the concentration of O-I_2 must decrease exponentially with time:

$$[o\text{-}I_2] \sim \exp(-\kappa t) \tag{7.10}$$

The comparison of this dependence with the experimental one shows that the beginning of reaction (several minutes) agrees well with mechanism (7.9) with $K=1.5\cdot10^{-2}$ Torr/min. Since the concentration of para $-I_2$ is practically constant during reaction, it can be said with confidence that mechanism (7.9) prevails over the radical-chain mechanism, for otherwise the exchange reaction between I atoms and para-I_2 molecules in the ground state which runs rather quickly would mix effectively the para-ortho modifications of I_2 molecules:

$$I + p\text{-}I_2 \rightleftarrows o\text{-}I_2 + I \qquad (7.11)$$

There is one more experimental fact that confirms that the contribution of radical-chain mechanism is very small. When a cell with a mixture of I_2 and 2-hexene is irradiated by the argon laser line at 488 nm, which is shorter than the dissociation limit, no distinct change is observed in the concentration of I_2. The non-coincidence of the whole experimental curve (see Fig.10) with dependence (7.10) may be explained by the fact that the reaction of 2-hexene iodization is of a higher order and occurs probably with the formation of a molecular complex /39/. The selective photochemical reaction of ortho-I_2 molecules studied in work /37/, that is a new-level repetition of experiment /40/ in prelaser selective photochemistry, can be directly applied to iodine isotope separation.

Zare et al /41/ have conducted successful experiments on photochemical separation of ^{35}Cl and ^{37}Cl isotopes through selective excitation of $I\,^{37}Cl$ molecules by CW dye laser radiation at 605.3 nm. Fig.11 shows the position of potential curves of the ICl molecule whose spectrum has been comprehensively studied in work /42/. This molecule does well for experiments on selective photopredissociation because of potential curve crossing at 18000 cm^{-1}, but in the experiments/41/ they excited the level $v'=18$ of the state A lying 784 cm^{-1} below the dissociation limit of the state X. The laser radiation only excited therefore the $I\,^{37}Cl$ molecules without resulting in their dissociation. The excited molecules were subjected to two reactions. In one case the $I\,^{37}Cl$ molecules reacted with trans- ClHC = CHCl forming cis-ClHC=CHCl with 10% - enrichment by the isotope ^{37}Cl. In the other case they reacted with 1,2 - dibromoethylene forming trans - ClHC=CHCl with 50% - enrichment by the isotope ^{37}Cl. In this work the product molecules were collected and analyzed using a gas chromatograph mass spectrometer combination specially designed for isotope ratio work.

Cl enrichment has also been achieved by selective excitation of Cl_2CS in mixtures with diethoxyethylene/43/. Mass spectral analysis of the remaining Cl_2CS after irradiation with either 465.78 nm Ar^+ or dye laser light showed the concentration of ^{35}Cl altered from its natural abundance of 75% to 64% or 80% depending on the isotopic species initially excited. The photochemical quantum yield in this system was shown to be as large as 0.5.

Photochemical isotope separation should be possible for a wide variety of elements. The problems and constraints of the method as well as its virtues are similar to those discussed for predissociation (section 5). Research on isotopically selective photochemistry should not only yield some practical separation processes but also a great deal of information on photochemical reaction mechanisms.

8. VIBRATIONAL PHOTOCHEMISTRY

The rate of a chemical reaction may be substantially enhanced by vibrational excitation of the reactant molecules. Gibert /44/ suggested this as a method for isotope separation in 1963. Gurs /45/ later hypothesized that by using an infrared laser source uranium separation might be achieved. In 1970 Mayer et al. /46/ reported deuterium enrichment following vibrational excitation of methanol-Br_2 mixtures with an HF laser. In a chemical reaction a bond in one of the reactant molecules is usually broken and a new bond formed to make products. It is thus natural to expect that vibrational excitation of the bond to be broken will cause the reaction to proceed more rapidly. If a large fraction of the energy of an exothermic reaction appears as vibrational excitation of the products, then the rate of the reverse, endothermic reaction, will be greatly increased by vibrational excitation /47-49/. In the last few years the effect of vibrational excitation on chemical reaction rates has been observed experimentally /50-69/ and treated theoretically in some detail /47,48,53/. More references appear in recent reviews /70,71/.

In this section we will discuss the important general features of the method for a very simple reaction scheme. Several possible methods of excitation are described. The kinetic scheme and practical limitations on isotope separation for the reaction HCl$(v = 2)$ + Br are discussed in detail. Other examples of atom-diatom reactions as well as several more complicated systems are presented.

A simple reaction scheme for isotopically selective photochemistry is shown.

$$AB + h\nu \longrightarrow A^{i}B^{\dagger} \tag{8.1}$$

$$A^{i}B^{\dagger} + C \xrightarrow{k_L} A + {}^{i}BC \tag{8.2}$$

$$A^{i}B^{\dagger} + M \xrightarrow{k_Q^M} A^{i}B + M \tag{8.3}$$

$$A^{i}B^{\dagger} + AB \xrightarrow{k_{VV}} A^{i}B + AB^{\dagger} \tag{8.4}$$

$$AB + C \xrightarrow{k_T} A + BC \tag{8.5}$$

The laser photons, hν, selectively excite a single isotope of AB to a particular vibrational level. These molecules react, (8.2), with reagent C. The laser-enhanced rate constant, k_L, applies to reaction of a particular vibrational level. Usually the rate constant will be the same for the $AB^{\dagger}$ produced in (8.4). Two relaxation processes, (8.3) and (8.4), compete with reaction (8.2). In (8.3), $A^{i}B^{\dagger}$ loses some or all of its vibrational excitation and no longer reacts with C at a rate equal or comparable to k_L. This decreases the quantum efficiency of the overall process. The collision partners, M, include the reagents AB and C as well as the products A and BC and any other species present in the system. When $A^{i}B^{\dagger}$ collides with AB, the AB molecule may be excited to the reactive state $AB^{\dagger}$, (8.4), and subsequently react by (8.2). The result is isotopic scrambling. This may be minimized by increases in the concentration of C relative to AB.

The thermal reaction between AB and C, (8.5), will produce products BC as long as the reagents are mixed. The thermal population of $AB^{\dagger}$, with vibrational energy E, is given by a Boltzmann factor and thus

$$k_L/k_T \leq \exp(E/kT) \tag{8.6}$$

To the extent that other states of AB react k_L/k_T will be smaller. Or put another way, in the very probable case that the vibrational excitation is not completely effective in reducing the activation energy k_L/k_T will be less than exp(E/kT). The non-selective product, BC, reaches a concentration k_T [AB][C]$t_{process}$, where $t_{process}$ is the total time during which the reagents are mixed. In many situations /72/ the value of k_L/k_T required is proportional to the separation factor needed and to $t_{process}$. This is a serious limitation on infrared photochemical schemes. If the excitation is by a single photon of CO_2 laser light near 1000 cm^{-1}, modest separations would be possible only if $t_{process}$ were in the microsecond range. If the reagents are to remain mixed for many seconds, several thousand cm^{-1} excitation energy is required. For many systems it will be necessary to reach overtone and combination levels. Theoretical analysis of the simple kinetic scheme above and of more complete schemes may be found in references /71-77/.

A wide variety of excitation processes may be used. The infrared active fundamental vibrations of a molecule may be excited by absorption of a single photon. (See sec. 4 for a discussion of thermal effects and the rotational energy transfer bottleneck.) Absorption coefficients are usually between 10^{-2} and 10 cm^{-1} $torr^{-1}$. Excitation of combination and overtone bands gives two or more quanta of vibrational excitation on absorption of a single higher energy photon. This may give larger values of k_L/k_T and may greatly increase the ratio k_L/k_{VV} (see below). The disadvantage is that the optical absorption cross sections decrease by nearly two orders of magnitude for each additional quantum of vibrational excitation.

Higher vibrational levels may also be reached by stepwise excitation through one or more intermediate levels /65,78/. This is particularly convenient when the molecule to be excited may be made to lase. Arnoldi and Wolfrum /65/ used an HCl laser to excite $H^{35}Cl$ from $v = 0$ to $v = 1$ and then to $v = 2$. If rotational relaxation is fast compared to the pulse length and if the laser energy approaches saturation, then a substantial fraction of the molecules which reach $v = 1$ will be pumped to $v = 2$. The scheme is clearly more practical than use of an optical parametric oscillator to pump $v = 0 \rightarrow v = 2$ directly. A large-scale, fastflow separator might utilize high-power c.w. lasers.

Raman excitation may also be used /58,61,69,79/. It is the only method for excitation of vibrations with zero transition dipole (e.g. homonuclear diatomics). Two lasers tuned such that their frequency difference is equal to the vibration-rotation frequency can strongly excite gases when powers approach 10^8 W/cm^2 /79/. Unfortunately, the overall conversion of laser energy to molecular excitation is not efficient. Raman excitation of N_2 has lead to isotope enrichment /61,69/.

The selective multiphoton excitation of vibrational levels discovered recently /1,2/ and especially direct observation of excitation of high vibrational levels at comparatively moderate intensities (10^6 - 10^7 W/ cm^2) /10-12/ give us one more and, probably, the only effective method for direct excitation of levels with their energy of several eV. Though the method is used now mainly for direct molecular dissociation, it can be applied, no doubt, with success to selective vibrational photochemistry of highly excited molecules.

Vibration-vibration energy transfer processes may occasionally be used to advantage. The fundamental level of a molecule may be excited, and subsequent

$$AB(v = 0) + h\nu \rightarrow AB(v = 1) \qquad (8.7)$$

$$2AB(v = 1) \rightleftarrows AB(v = 2) + AB(v = 0) + \Delta E \qquad (8.8)$$

$$AB(v = 2) + AB(v = 1) \rightleftarrows AB(v = 3) + AB(v = 0) + \Delta E \qquad (8.9)$$

V → V transfers (8.8 & 8.9) will populate higher levels. Because of anharmonicity these reactions are exothermic and at low translational temperatures have equilibrium constants much greater than 1. Thus, molecules are pumped up to high vibrational levels/74,77,80/. In such a system the ΔE's for heavy isotopes favor their excitation even more strongly.

$$AB(v = 1) + {}^{i}AB(v = 0) \rightleftarrows AB(v = 0) + {}^{i}AB(v = 1) + \Delta E \qquad (8.10)$$

$$AB(v = 1) + {}^{i}AB(v = n) \rightleftarrows AB(v = 0) + {}^{i}AB(v{=}n{+}i) + \Delta E \qquad (8.11)$$

In fact, the laser excitation need not even be isotopically selective /61/. Isotope separation in $N_2 - O_2$ mixtures has been reported for vibrational excitation with an electrical discharge /81/. Dubost, Charneau, Abouaf-Marquin and Legay /82/ have excited CO dilute in Ar at temperatures near 10° K. Excitation of ${}^{12}CO$ by a frequency-doubled pulsed CO_2 laser, was followed by V → V energy transfers. In times less than 1 msec energy was transfered to higher vibrational levels and to heavier isotopes. In samples with concentrations of natural abundance CO in Ar between 0.003 and 0.01 there were more ${}^{13}CO$ and $C^{18}O$ molecules excited than ${}^{12}C^{16}O$. The selectivity is greater than 100. Vibrational levels as high as v = 7 were observed. There are clearly possibilities for selective reaction with such high excitation. Under most circumstances the effect of V → V transfers Eq.(8.4) will be to destroy the isotopic selectivity provided by the laser rather than to create a selectivity not provided by the laser.

Energy transfer from vibration into translation and rotation destroys all of the selectivity of the laser excitation, both with regard to isotope and chemical species. Even though this excitation is completely thermal, reaction products may be quite different from those obtained by heating the vessel walls. This is particularly true when a c.w. laser beam of a few mm diameter passes through a cell of a few cm diameter containing pressures of a few torr or greater. Many experiments have been performed under such conditions /46,51,52,75/. In such a case the gas in contact with the wall remains cool while the center may be heated above 1000°K /83-85/. The rates of homogeneous gas phase reactions are accelerated while wall-catalyzed reactions are unaffected.

The isotopic separation using the process

$$H^{i}Cl(v = 2) + Br \rightarrow HBr(v = 0) + {}^{i}Cl \qquad (8.12)$$

$${}^{i}Cl + Br_2 \rightarrow {}^{i}ClBr + Br \qquad (8.13)$$

provides an excellent example of isotopic separation kinetics /65,66/. Competing processes of interest include:

$$H^{i}Cl(v = 2) + Br \rightarrow H^{i}Cl(v = 1) + Br \qquad (8.14)$$

$$\rightarrow H^{i}Cl(v = 0) + Br \qquad (8.15)$$

$$H^{i}Cl(v = 2) + HCl(v = 0) \rightarrow H^{i}Cl(v = 1) + HCl(v = 1) - 102cm^{-1} \qquad (8.16)$$

$$HCl^{\dagger} + M \rightarrow HCl(v = 0) + M \qquad (8.17)$$

$$H^{i}Cl(v = 2) + HCl(v = 0) \rightarrow H^{i}Cl(v = 0) + HCl(v = 2) \qquad (8.18)$$

$$HCl^{i}(v = 1) + HCl(v = 0) \rightarrow H^{i}Cl(v = 0) + H\ Cl(v = 1) \qquad (8.19)$$

$$HCl(thermal) + Br \rightarrow HBr + Cl \qquad (8.20)$$

Rates have been measured for many of these processes /64,66/. The rate constant for removal of HCl(v = 2) by Br is given by

$$k_{12} + k_{14} + k_{15} = 1.8 \times 10^{-12}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{sec}^{-1} \qquad (8.21)$$

Of this total approximately 70% is (8.14). The remaining 30% is most probably the desired reaction (8.12). Thus 30% is an absolute upper limit on the quantum yield. The quantum yield is further decreased by processes (8.16) and (8.17). The rate of (8.16) places an upper limit on useful values of the ratio of HCl to Br concentration. Since

$$k_{16} = 3.3 \times 10^{-12}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{sec}^{-1}, \qquad (8.22)$$

Br pressures should be at least double the HCl pressure. For (8.17) the most important collision partner is Br_2;

$$k_{17}^{Br_2} = 3.3 \times 10^{-14}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{sec}^{-1}$$

for HCl(v = 1) and is probably about twice this value for the v = 2 → 1 transfer. Br concentrations should therefore be greater than 2% of Br_2. The rate of the isotope scrambling reaction (8.18) has not been measured. Since it involves the exchange of two vibrational quanta in one collision, it will probably be at least one order of magnitude slower than (8.19) for which

$$k_{19} = 1.9 \times 10^{-11}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{sec}^{-1} \qquad (8.23)$$

In a system where the concentration of v = 0 and v = 1 are comparable isotopic scrambling by (8.19) followed by the reverse of (8.16) gives natural HCl(v = 2) which then reacts by (8.12) to scramble the separation. The thermal rate k_{20} may be calculated from the measured rate of Cl + HBr and the equilibrium constant

$$k_{20} = 3 \times 10^{-23}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{sec}^{-1} \qquad (8.24)$$

Thus k_{12}/k_{20} is greater than 10^{10}.

Arnoldi, Kaufmann and Wolfrum/65/ report separation factors greater than two for this reaction system. They used an HCl pulsed chemical laser to sequentially excite from v = 0 to v = 1 to v = 2. For equal pressures of Br and HCl a separation factor of 2 was observed. This sets the limit for k_{18}

$$k_{18} \leq k_{12} + k_{14} + k_{15} + k_{16} = 5 \times 10^{-12}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{sec}^{-1} \qquad (8.25)$$

The efficiency of the processes with respect to the infrared laser is limited by the ratio $k_{12}/(k_{14} + k_{15})$, by the ratio $k_{12}(\text{Br})/(k_{16} + k_{18})(\text{HCl})$ and by the molecules excited only to v = 1 and not on to v = 2. For good separation Br atoms should be at higher pressure than HCl. Effective use of this reagent requires excitation of a substantial fraction of the desired isotope. An upper limit on total reagent pressures will be set by

$$\text{Br} + \text{Br} + \text{M} \rightarrow \text{Br}_2 + \text{M} \qquad (8.26)$$

In many cases it will be useful if the laser pulse duration is long compared to the chemical lifetime of HCl(v = 2), $[(k_{12} + k_{14} + k_{15})(\text{Br})]^{-1}$.

To complete a useful separation the reagents and products must be physically separated at a low cost before the system returns to thermodynamic equilibrium. The scavenging reaction (8.13),

$$k_{13} = 1.2 \times 10^{-10}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{sec}^{-1} \tag{8.27}$$

is so fast that there is no problem with competing processes such as:

$$^{i}Cl + HCl \rightarrow H^{i}Cl + Cl \tag{8.28}$$

$$^{i}Cl + HBr \rightarrow H^{i}Cl + Br \tag{8.29}$$

On the longer timescales, 10^{-2} to 10^{2} sec, of distillations or selective condensation from the reaction mixture, care must be taken to prevent thermal reaction (8.20) and both homogeneous and wall-catalyzed reversal of the separation by processes such as

$$^{i}ClBr + HBr \rightarrow HCl + Br_2. \tag{8.30}$$

It is likely that the attempt/66/ to isolate enriched ^{37}Cl using this system failed because of (8.30). It should be noted that surface catalysis often gives changes in activation energy much larger than can be induced by single infrared photons.

Raman excitation of nitrogen in air at liquid nitrogen temperature has been reported by Basov et al./61,69/ to produce NO enriched 100 times in ^{15}NO. This might result from

$$N_2^{\dagger} + O \rightarrow NO + N \tag{8.31}$$

An electrical discharge produces NO enriched by 10 times /81/. The V → V energy transfer pumping mechanism is presumed to cause the selectivity.

More complex chemical reactions have been induced by infrared lasers /57,59,67,68/. In one case pumping of BCl_3 molecules by a focussed pulsed CO_2 laser, which probably excites high vibrational levels (see § 6), separation of boron isotopes was achieved /86/. In the reaction $BCl_3 + H_2S$ (or D_2S) 15% enrichment of ^{10}B in 10 hours irradiation was found. The reaction of CH_3OH-CD_3OD mixtures with Br_2 induced by a c.w. HF laser was reported to be isotopically selective/46/. Several aspects of these results have been criticized and the report has not been confirmed. Careful studies of the dependence of rate on vibrational excitation have been done for /57,59/

$$NO + O_3 \rightarrow NO_2 + O_2 \tag{8.32}$$

The attractive feature of vibrational photochemistry for isotope separation is the promise of using low energy IR photons from an efficient molecular laser to get a good yield of product. Since 1 mole of photons at 3,000 cm^{-1} is 10^{-2} kWh and some IR lasers are about 10% efficient, processing of bulk chemicals might even be economic. There are many problems to overcome: thermal reaction rates, vibrational energy transfer, surface catalyzed reactions, fixed frequency sources and so on. The methods which rely on V → V transfer to enhance the excitation of heavy isotopes /61,69,74,77,82/ appear quite promising for systems with anharmonicities and isotopic shifts larger than kT at temperatures where the vapor pressure is sufficient. C,N and O are excellent possibilities. Heavier elements such as S appear less promising. For heavier elements the high field selective infrared excitation and dissociation (Sec 6) appear most promising at this time.

9. Atomic photodeflection

Selective deflection of atoms of a particular isotope is based on the effect of resonant light pressure on gases discovered by P.N.Lebedev /87/ or, from the quantum standpoint, on the effect of momentum transfer $\hbar\omega/c$ as an atom absorbs a $\hbar\omega$ photon. The value of atomic velocity build-up in the direction of the photon is much smaller than the average thermal velocity. For example, when a photon is absorbed at the D-line of Na, Δv = 2 cm/sec. Therefore experimentally this effect can be observed using a well-collimated atomic beam with its transverse velocity $v_\perp \gtrsim \Delta v$, the collimated light beam perpendicularly oriented. Photodeflection of atoms (Na) in a beam was first observed in a very fine experiment as far back as 1933 in work /88/. With the advent of tunable lasers this effect became not only observable but also the subject of discussion on its application to isotope separation on a practical scale. It is probable that the first suggestion on the use of light pressure in selective pumping of gases, including those of a particular isotopic composition, was put forward in work /89/. The separation scheme suggested in this work employs not only atomic beam deflection but also the effect of selective light pressure in low-pressure gases in a two-chamber vessel (Fig.12 a). Laser light acts as an optical pump pushing forward resonant atoms (circles) into chamber 1 without acting on nonresonant atoms (points). As a result, the concentration of resonant atoms appears to be somewhat higher in chamber 1 than in chamber 2. Later isotope separation by the use of light pressure was suggested both for beam geometry (in works /90,91/) and mixtures (in work /90/).

Assume that an atom absorbs the resonant radiation from a collimated light beam and then reemits it isotropically in any direction. Then in the light beam direction it is acted upon by the force:

$$F = \frac{I\sigma}{\hbar\omega c}|a_1|^2 - \frac{I\sigma}{\hbar\omega c}|a_2|^2 , \qquad (9.1)$$

where I is the beam intensity, σ is the resonant absorption cross-section, $|a_i|^2$ is the probability of atomic occupation in the i-th level of a resonant-with-field transition. If the field intensity is high enough, $|a_i|^2$ approximates 1/2 , whereas their difference tends to $\left(|a_1|_0^2 - |a_2|_0^2\right)\left(1 + \frac{I}{I_{sat}}\right)^{-1}$, where $I_{sat} = \frac{\hbar\omega\gamma}{2\sigma}$ is the intensity of transition saturation depending on the γ- rate of particle relaxation from excited state 2 to ground state 1. So, with I >> I_{sat} and $|a_i|_0^2=1$ the force acting on an atom tends to the constant:

$$F_{max} = \frac{\hbar\omega}{2c}\gamma \qquad (9.2)$$

The physical meaning of expression (9.2) is very simple. During each photon reemission the atom acquires a momentum with $\hbar\omega/c$. The number of such reemissions is determined by the γ rate of atom relaxation to the ground state, and the multiplier 1/2 appears due to the fact that the atom spends one half its time in ground state 1.

If an atom interacts with a light beam of a diameter during $\tau_0 = a/v_0$, it acquires the velocity Δv in the light beam direction and is deflected at the angle $\Delta\varphi$

(Fig. 12 b):

$$\Delta\varphi = \frac{\Delta v}{v_0} = \frac{\gamma d}{2c}\,\frac{\hbar\omega}{Mv_0^2} \simeq \frac{\gamma d}{2c}\,\frac{\hbar\omega}{kT_0}, \quad (9.3)$$

where v_0 is the average atomic velocity in a beam determined by the temperature T_0 of the atomic beam source. For allowed transitions with $\gamma = 10^8$ sec^{-1}, $d = 1$ cm, $T_0 = 10^3$ °K and 2 eV an atom in a light beam can execute 10^3-10^4 photon re-emissions and be deflected at the angle $\Delta\varphi \simeq 4^\circ$, that is quite observable. It is evident that, for observation to be possible, the angle divergence of atomic beam φ_0 should not exceed the angle of deflection $\Delta\varphi$.

The first successful experiment on isotope separation by means of atomic photodeflection was run in work /92/ with a beam of barium atoms used. The resonant transition $6s^2\ ^1S_0$ - $6s6p\ ^1P_1$ at 553.5 nm was used; its isotope hyperfine structure is extremely small /93/. The addition of neutrons to the filled neutron shell (in the sequence of isotopes from ^{134}Ba to ^{138}Ba) with the magic number N=82 changes the nuclear charge distribution very little and so the isotope shift is extremely small. The hyperfine structure components for the line of BaI are divided by an interval of no more than 30 MHz, that is much smaller than the Doppler width which is 10^3MHz. Therefore, to produce isotopic selectivity of excitation, an atomic beam should be used (the degree of beam collimation is about 1/200). The lifetime of the excited state $^1P_1$ is 8.4 nsec, and in the time of light beam crossing $\tau_0 \simeq 10^{-4}$ sec an atom must reradiate photons from the beam, which causes transition saturation, 10^4 times. Actually this does not occur because Ba atoms have a high probability for radiative transition from the excited state $^1P_1$ to the lower metastable state $^1D_2$. The ratio between probabilities of return to the ground and metastable states equals 60, and so the maximum increase of atomic transverse velocity due to light pressure is equal to $60\frac{\hbar\omega}{Mc}$ = 45 cm/sec. Such selective deflection of Ba atoms during selective excitation of a particular isotope has been observed through mass spectral analysis of deflected atoms. Fig. 13 presents some results of experiment /92/ ^{138}Ba (71.66%) is the main isotope of Ba in the natural mixture. During selective excitation of ^{137}Ba one can observe an increase of its mass peak, while during selective excitation of a component of the hyperfine structure of ^{136}Ba an increase in the mass peak of ^{135}Ba can be observed simultaneously that points to overlapping of two spectral components.

An apparent disadvantage of the photodeflection method is that an energy $\hbar\omega$ should be consumed to deflect an atom by a small angle, that is, to increase its energy by a negligible value equal to the recoil energy which in the relation $\hbar\omega/2Mc^2$ is smaller than the photon energy. Therefore in work /94/ a method is proposed for effective return of the energy absorbed by atoms. In this work atomic excitation and its return to the ground state are done by the method of fast adiabatic passage under the action of two counter-running light pulses with variable frequency. The first pulse whose frequency scanning (chirping) rate through the atomic absorption line complies with the condition /95,96/:

$$\left|\frac{d\omega}{dt}\right| \ll \left(\frac{\mu\mathcal{E}}{\hbar}\right)^2 \qquad (9.4)$$

transfers the atom into the excited state with transfer of the momentum $\frac{\hbar\omega}{c}$, and the counter-running pulse carries back the atom to the ground state in the same stimulated (not spontaneous) way with transfer of the same momentum. It is assumed that a considerable profit in energy can be obtained provided the conditions for using a considerable portion of pulse energy when propagating along a sheet atomic beam are met /94/. The authors of work /92/ are optimistic about energy consumption in the method of photodeflection for isotope separation as well as about the elaberation of the method for isotope production on a commercial scale. This opinion, however, should be taken with care since the method of light photodeflection demands that matter should be prepared in a very specific state, that is, in the form of a well-collimated atomic beam in high vacuum, in addition high-quality coherent light with controlled parameters should be used. The main thing in this case, of course, will not be expenditure of energy but the price of the equipment for producing atomic beams and highly coherent laser light.

10. Economics and Engineering of Laser Isotope Separation.

The isotopic enrichment of ^{235}U for electrical power generation in nuclear reactors is by far the most economically important objective of laser isotope separation. World fuel requirements for nuclear reactors between now and the year 2000 are estimated to be approximately 6 million tons of U_3O_8. Enrichment cost estimates for processing this ore amount to approximately 150 billion $USA. An efficient laser enrichment scheme could cut these costs to a small fraction of this amount. Large quantities of D_2O are needed for heavy water nuclear reactors. The current world production capacity of somewhat greater than 10^6kg/yr is probably not sufficient. However, it is hard to conceive of a laser separation process costing less than the current price of $1 per mole D atoms (or $1 per 10 Gr. D_2O).

The simple and effective method of isotope separation with IR radiation of low-price CO_2 lasers discovered recently (§ 6), which probably can be applied to separation of hydrogen and deuterium isotopes, has offered possibilities of solving this problem as well. The economic importance of separating isotopes of other elements with laser methods is neither so obvious nor so pressing as that for ^{235}U. The total annual world sales of separated isotopes other than ^{235}U or D is less than $5 million. The importance of enriched isotopes of other elements lies not in present uses but in the possibility of new uses in science, medicine and technology, uses which are likely to develop only if high volume, low cost sources of isotopes are available.

The economic and industrial scale of the ^{235}U enrichment problem is beyond the scope of the normal consideration of laboratory scientists and therefore deserves some additional perspective here. In considering the urgency of this problem it is well to bear in mind that the cost of enrichment today is approximately 6% of the total cost of nuclear power production. $150 billion over 25 years is not so large when compared to the recent $50 billion increase in the price of oil sold in one year. Nevertheless the magnitude of the challenge to research scientists, to engineers and to industry to develop some of the untested scientific ideas described above into practical methods, from there into pilot plants and on to a multibillion dollar industry is enormous. Success is by no means certain. The magnitude of the industry can be illustrated with a few figures from the U.S. nuclear industry. A typical light water reactor produces 10^9 watts. It requires processed fuel from 600 tons of U_3O_8 ore for an initial charge and an annual use of 200 tons. The fuel is enriched to about 3% ^{235}U from a natural abundance of 0.75%. The depleted ore is discarded with 0.2 to 0.3% ^{235}U remaining. The enrichment is carried out in large gaseous diffusion plants. One such plant handles about 20,000 tons of UF_6 annually. Such a plant consumes 2.4×10^9 watts of electricity. The construction cost of the plant is about $2.8 billion and the power plants to go with it about $1.5 billion. The U.S. currently anticipates the need to put new plants of this magnitude into operation each 18 months beginning in 1984. Such a plant is now being built in France. There are several countries perfecting gas centrifuge technology. This may cut enrichment costs by 10-30%. The Becker nozzle process has entered the pilot plant stage and in time might lead to significantly lower costs, perhaps a factor of two.

The potential of laser processes for cost reduction is illustrated by the fact that gaseous diffusion uses 5 MeV of electrical energy for separation of each ^{235}U atom. The overall enrichment cost is about $5. per gram ^{235}U.

The energy requirement for a laser process can be less than 10 eV of photons per atom of ^{235}U, a few keV of electricity for standard visible laser efficiencies. Chemical processing of the ore or vaporization of solid samples requires a similar amount of energy, 5-10 eV divided by the natural abundance of 0.0075. The power costs of an ideal laser system would be negligible. However, to produce the 90 tons of ^{235}U per year, a perfectly efficient use of photons at 500 nm requires an average power of 3kW. Realistically tens of kW will be needed. Existing tunable laser systems in the visible operate with only a few watts of power and systems in the ultraviolet are even less powerful. A great deal of laser engineering or preferably some fundamentally new laser systems are crucial to the ultimate success of laser separation of uranium. If such lasers can be built for orders of magnitude less than the cost of diffusion plants, not only will laser enrichment be very cheap but we may have some very useful laser systems for other areas of science and technology. The very high selectivity inherent in most laser separation schemes makes it likely that the ^{235}U discarded with the ^{238}U would be greatly reduced. This would reduce the requirement for new ore by as much as 40%.

At the present time it is not at all clear which method of laser separation of uranium will be the least expensive. An infrared photochemical method requiring only the use of one of the efficient lasers already developed could be very cheap indeed. However, no such scheme currently appears to be feasible. The two-photon ionization method can clearly be used to enrich uranium. But the cost of such a system for commercial production could be very high. It is clear that a great deal of research on possible methods is needed in order to select the best one. It is likely that the first laser method to go into commercial production would not be the final one.

To reduce the price of heavy water production is of great importance /98/. Today the cost of heavy water (100 dollars/kg) amounts to 25% of the total cost of a heavy-water reactor ($100 million/1,000 tons). If the cost of deuterium enrichment is reduced by several times, it will be economical to construct natural-uranium and heavy-water reactors.

The economics of production of a variety of stable isotopes is illustrated in Table 1. For the relatively small amounts of material produced other than uranium and deuterium the most efficient methods are fractional distillation or counter current chemical exchange for the lighter elements and magnetic deflection (mass spectroscopy) for the heavier ones/99/.For laser separation a lower limit on cost is set by the photon energy used. This is only 0.1 kWh for one mole of photons at 3,000 Å. If the overall efficiency of conversion from electrical energy to laser photons and finally to separated product is 10^{-3}, then the electrical energy cost per mole is about \$1. In the near future and for small scale production the capital cost of lasers and the cost of labor will doubtless be far larger than energy costs. Nevertheless the possibility of large reductions in isotope cost is clear.

Work on formaldehyde suggests two situations where laser enrichment may most easily be applied to advantage. The rare isotope ^{17}O is intermediate in mass between ^{16}O and ^{18}O. As a result distillation techniques do not produce cleanly separated material. Formaldehyde predissociation could provide an effective method of removing ^{17}O from mixtures enriched by distillation. Another application could be to increase the sensitivity of ^{14}C dating. The carbon in the sample to be dated would be converted to formaldehyde ar selectively laser photolyzed to convert all $^{14}CH_2O$ to ^{14}CO and leave behind a maximum amount of $^{12}CH_2O$. Both of these applications would become economically feasible at process costs which would be too high for mass production of ^{13}C or ^{18}O.

In view of the extensive research required for the development of methods of separation for any one element and the likelyhood that the optimum process will be different for each element, it is important to identify now those isotopes which are most likely to be of value in new applications. Some applications for C, N and O are already being explored since their prices are relatively low. C and O could be used as monitors of body functions such as metabolism. Nitrogen depleted ^{15}N is being used in fertilizer tracer studies at the University of California, Davis. Labeled natural products may be prepared by feeding simple ^{13}C, ^{15}N or $^{17,18}O$ containing food to plants or animals. Such work traces biochemical pathways and can produce labelled compounds almost impossible to make in the laboratory. The isotopes ^{13}C and ^{18}O may be used extensively in CO_2 lasers in two aspects. ^{13}C may be successfully used in simple laser devices for measurements of the isotope ratio $^{13}C/^{12}C$ ($^{12}CO_2$ and $^{13}CO_2$ lasers) /100/ which find wide application in geology for oil prospecting. Carbon and oxygen isotopes may be used in CO_2 lasers with electric discharge /101/ and optical /102/ pumping to widen the region of frequency tuning. The isotope ^{40}K, that is a natural radioactive isotope, is necessary for agricultural investigations. We suspect that the production of some important materials such as ^{34}S, ^{57}Fe, ^{48}Ca, etc. will be developed provided their cost is reduced by several orders of magnitude. We should mention the problem of isotope separation recently considered by Gross /103/, the isotopes which are important for nuclear metallurgy, ^{50}Ti in particular, as important construction material for nuclear reactors.

TABLE 1. Current Stable Isotope Prices (approximate)

Isotope	Natural Abundance %	Enriched Abundance	Price (US $/mole)	Method
D	0.015	99+	1	Chemical Exchange
^{13}C	1.11	96	10^3	Distillation
^{17}O	0.037	40	10^5	Distillation
^{37}Cl	25	90	6×10^4	Calutron[a]
^{48}Ca	.185	95	10^6	Calutron
^{57}Fe	2.19	90	2×10^5	Calutron
^{79}Br	50	99	3×10^5	Calutron
^{196}Hg	.15	48	10^8	Calutron
^{235}U	.75	3	10^3	gas diffusion

[a] Mass Spectrometer at Oak Ridge, Tenn., U.S.A. /99/

11. Conclusion

In the present review we have made an attempt to consider systematically the main methods of laser isotope separation already demonstrated in research laboratories. They form the basis for further progress not only in science but also in industry. We hope that in the near future other methods will be elaborated since nowdays, when the energy crisis begins affecting the living standard of peoples and the progress in technology, some scientists in many countries consider studies into laser isotope separation to be an urgent and important problem. Recently, when our review was being written, several interesting papers had been published making a good start to new methods. Lately, for example, the first isotopically selective photochemical reaction of dissociation has been conducted in a solid phase at low temperatures /104/. Quite recently some schemes have been proposed for isotope separation based on heterogeneous chemical reactions /105/, condensation of vibrationally excited molecules /106/, deflection of vibrationally excited molecules in a nonuniform electric field /107,108/, possible selective molecular ionization with IR radiation /109/, etc. We think it would be untimely to discuss these methods in more detail here before their experimental careful checking, so we limit ourselves with this mention only.

Finishing the review we would like to stress that the methods of selective photophysics and photochemistry being developed for laser isotope separation will far exceed the limits of this problem from the principle and practical standpoints. In essence, the question is a new approach to materials technology at the atomic-molecular level where one may manipulate directly with atoms and molecules of particular sorts using a laser, that is, produce macroscopic amounts of matter "by one atom, by one molecule". Let's discuss briefly the possibility of laser production of highly pure substances, laser separation of nuclear isomers and selective detection of single atoms and molecules as such wider applications.

Production of pure substances. To produce a highly pure substance by the methods of selective laser photophysics we can apply selective ionization of atoms and selective dissociation of molecules. The first method seems to be rather promising since it is very, universal and flexible.

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 $\mathcal{E}_{ion} \simeq 7$-$8$ eV and the light beam cross-section is of 1 cm^2 this corresponds to about 1/2 mole 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 dye lasers may by considered as a rather efficient method of fine separation of substances at atomic level.

Laser purification of substances by the selective ionization method /110/ is no different from isotope separation in the principle of operation but necessitates a higher coefficient of separation (enrichment) within one cycle, 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 compared to existing methods of substance purification based on the difference between specific chemical and physical properties of substances under purification and impurities.

Firstly, the method has an extremely high potential 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}% be 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 no matter what its physical and chemical properties (temperature of fusing and boiling, reactivity, etc.) can be selectively ionized by properly choosing 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 directly producing substances in form of films as well as those of complex composition. The ion beam may be directed over the surface of the substrate to produce a pure film (see Fig. 14). Independent selective ionization of two or three different elements at a time in different beams and collection of their ions on the same substrate 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 ionization, ion extraction from a beam and their deposition on the substrate may be accomplished in a high vacuum. It doesn't require a contact between the substance under purification and any reagent or material, except for a substrate for which a material without unwanted impurities may be used.

The development of 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 higher.

Separation of radiactive isotopes and nuclear isomers.

Selective laser photophysics methods have an extremely high selectivity and allow manipulation of atoms by means of light and electric fields without direct contact. So, in perspective it is possible to apply these methods for technology at atomic-molecular level of waste of radioactive industry (nuclear reactors). It is important not only for technology, but also it is a quite new approach for preparation of inversion of nuclear level populations by using laser separation of excited (isomer) and unexcited nuclei /111/. It is possible to hope for an important contribution of selective laser photophysics methods to the γ-laser (status of this problem has been considered in works /112,113/).

The estimates given in work /114/ show that, to realize this way of development of the γ- laser, we should prepare a concentrate of excited nuclei during a fairly short time (10^{-2} - 10^{2} sec), though the absolute amount of a radioactive substance may be as small as 10^{-8} gr. The necessity of preparing a concentrate of excited nuclei forces us to give up the schemes that directly use the excitation of the sample itself. In this case it is difficult to obtain simultaneously nuclear-level population inversion and the excitation of a significant fraction (several percent) of one sort of nuclei relative to all the other sorts in the target. It seems expedient to use selection of the nuclei of desirable composition in the excited level.

Fig.15 shows a possible theoretical scheme of the γ -laser which complies with the stated requirements. When the target is bombarded by a stream of neutrons, a relatively small number of excited nuclei is produced. The excited nuclei are extracted from the target by, for example, rapidly vaporizing the target with a pulse of laser radiation. The next problem is how to extract rapidly the nuclei of a given composition in the excited state. For this purpose, the method of selective photoionization of atoms is, in our opinion, suitable. The existence of the isomeric structure in atomic spectra allows selective laser excitation of only atoms with excited nuclei of a particular composition. For this purpose the wavelength λ_1 of the laser should coincide with the optical absorption line λ_0^* belonging to the atom with an excited nucleus M* of the desired composition. The subsequent separation of the excited atoms $\tilde{A}$ (M*) is accomplished by photoionizing them with an auxiliary laser pulse. After the simultaneous irradiation of the products of vaporization of the target by laser radiation at two wavelengths λ_1 and λ_2, ions $J(M^*)$ of a given isomer M* only are produced which can be gathered by the electromagnetic focusing system and deposited on a charged filament.

The limitation on gas density due to resonant charge exchange leads to a limitation on the maximum number of atoms which can be sorted per unit time. The estimates presented in work/114/ show that the scheme of γ- laser (Fig.15) with laser sorting of excited nuclei through selective photoionization is quite realizable with real physical parameters.

Selective detection of atoms and molecules. The methods of selective laser photophysics may solve the problem of physical extraction of chosen specific sort of atom or molecule from a mixture of other atoms (or molecules) which have the same chemical properties. Of course, a first and more simple part of this problem is selective detection of single atoms and molecules. In particular, for this aim it is especially convenient to use the method of selective two-step photoionization. Attention was given to this fact even in the first work /115/, and then it was stressed in /116/.

The method is particularly simple in the case of atoms. As shown in § 3, selective excitation and subsequent photoionization of each particular atom in the mixture is secured by the selection of not only proper frequencies but also intensities of laser beams. This method, in principle, may provide detection of single atoms, but, unlike that of fluorescence, it is a "destructive" method of detection. It is advisable to use it, for instance, to detect atoms in metastable states the probability of fluorescence for which is small and relatively a low power is needed for photoionization (especially with an external electric field present). It goes without saying that the photoionization method of selective atomic detection has a very important advantage over all other methods, that is its ability to extract a detected atom with the aid of external electric and magnetic fiels.

After the first experiment on selective ionization of Rb atoms had been conducted in our work /115/ (§ 3), the method was successfully applied in work /117/ to detect Na atoms in a beam. It is clear that the elaboration of methods of selective photoionization to separate isotopes and purify substances will give birth to the new spectroscopic method of detection and extraction of particular atoms from a mixture.

Selective ionization of molecules by laser radiation is in principle of particular importance. The point is that the problem of detecting microscopic amounts of molecules by physical methods is quite difficult and practically has not been solved for complex molecules /118/. The mass-spectral analysis is now a common method for detection and identification of complex molecules but its sensitivity is inadequate and there is practically no selectivity of detection for complex molecules which differ only in spatial structure. Therefore the development of new methods to solve this problem is very urgent to-day. The method of selective molecular ionization by laser radiation may be used as the basis for the so-called laser mass-spectrometer /119,120/. A laser with the tunable frequency ω_1 excites selectively the vibrational (and electronic for certain molecules) state of molecules. Due to such an excitation the edge of the molecular photoionization band lying usually in the VUV region is shifted by a small magnitude. The second (VUV) laser brings about molecular photoionization, and its frequency is selected in the area of a maximal slope of the photoionization band edge. In this case preliminary selective excitation of the molecules by the tunable laser even by comparatively a small value ($E_{exc.} \simeq 0.1 - 0.5$ ev results in a marked change of the photoionization cross-section $(10^{-1} - 10^{-2}$% with regard to the molecular distribution over the rotational states), that is a change in the photocurrent. Photoions are sent then into a common mass-spectrometer which measures the mass spectrum, i.e. $i = f\,(^{M}/e)$. In addition to this, with this version of mass-spectrometer we can measure the photocurrent magnitude for a given value of $^{M}/e$ as the function of the tunable laser frequency ω_1. In this case the IR spectrum of microquantities of complex molecules is measured since, with the ω_1 frequency and that of molecular absorption coincident, the molecules pass into the excited state and hence the ionic photocurrent amplitude varies. The laser mass-spectrometer with selective molecular ionization, instead of the usual nonselective ionization by an electron beam (or by continuous VUV radiation), will produce at the same time the optical (IR and visible) spectrum of absorption and the mass spectrum. This method enables one to obtain information on the spatial structure of molecules with the same mass, etc. The first successful sxperiments on molecular photoionization carried out in work /121/ using a simple and efficient VUV H_2 laser at 1600 Å /122/ demonstrate the practicability of such laser selective detectors for complex molecules.

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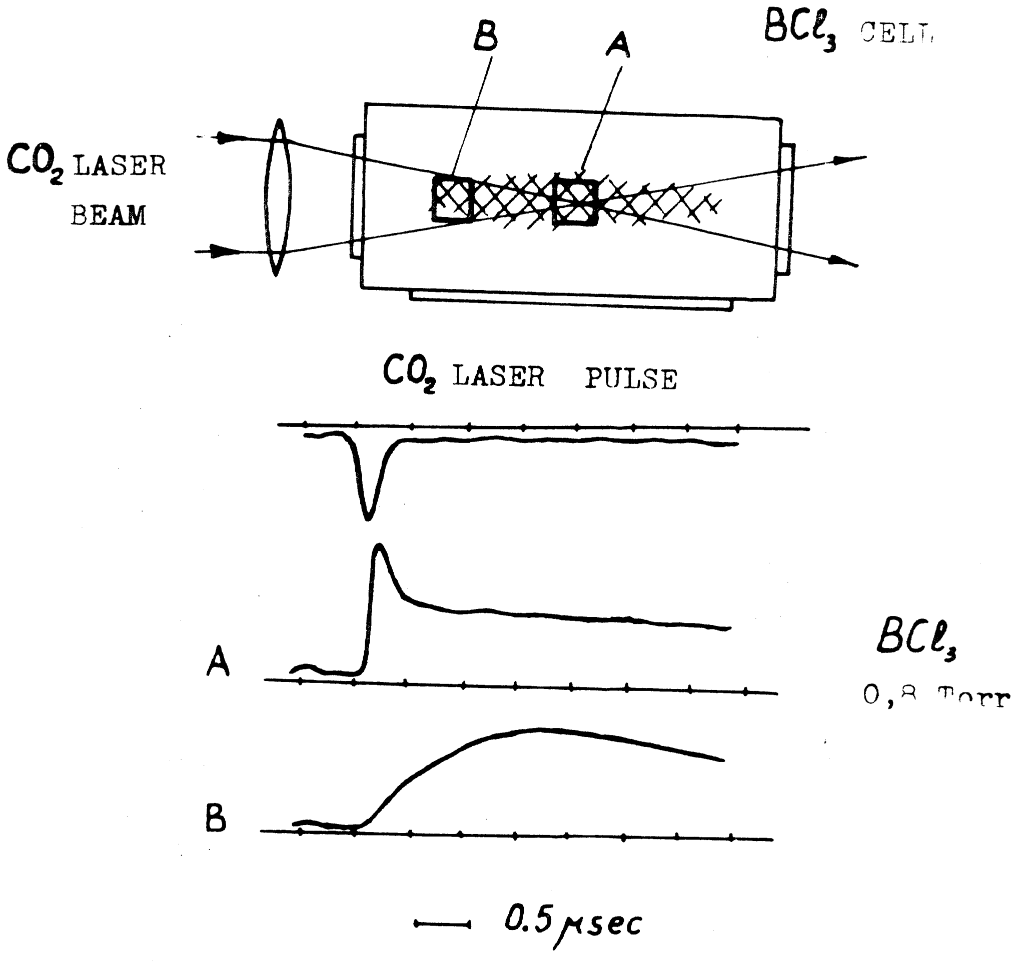
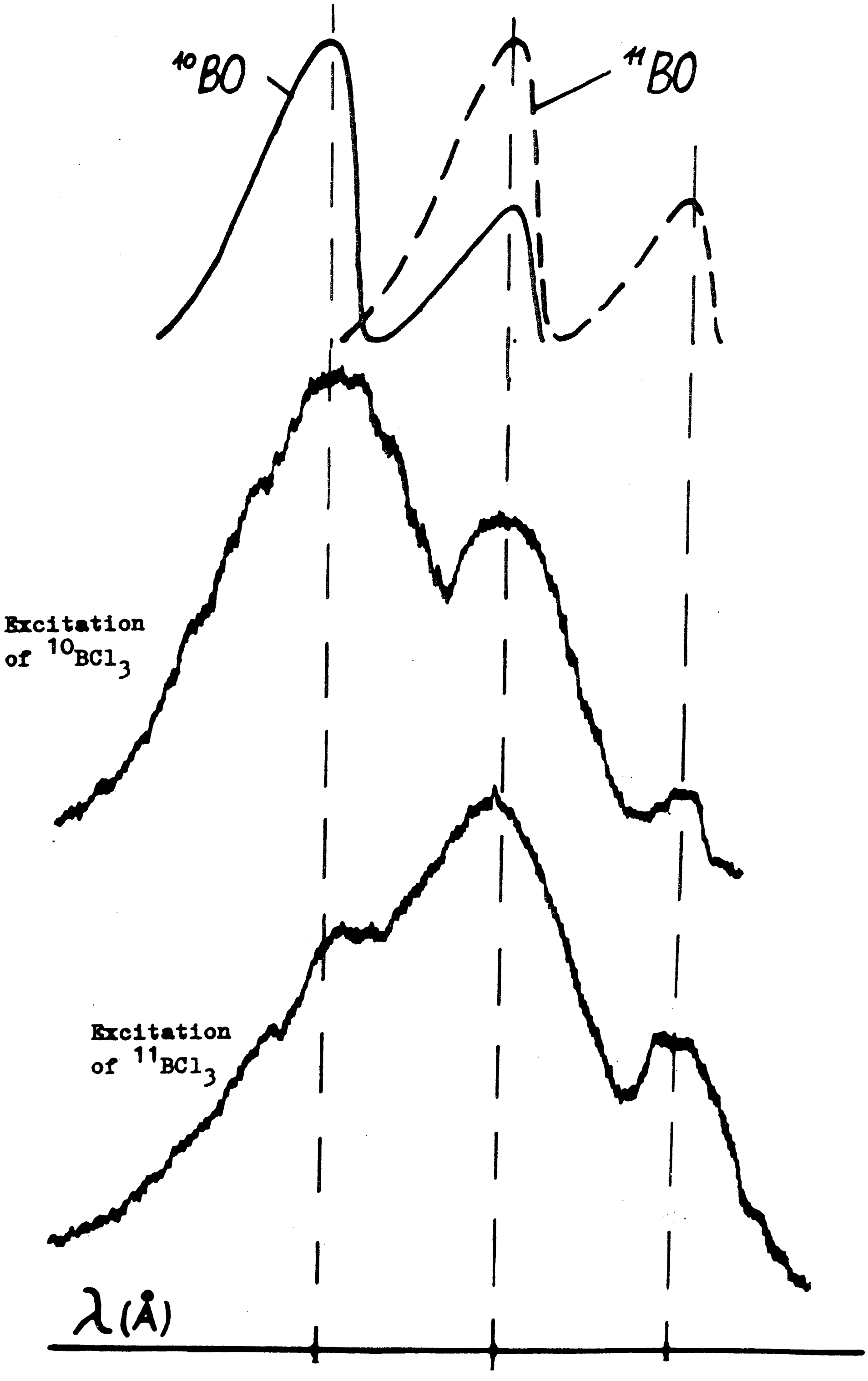


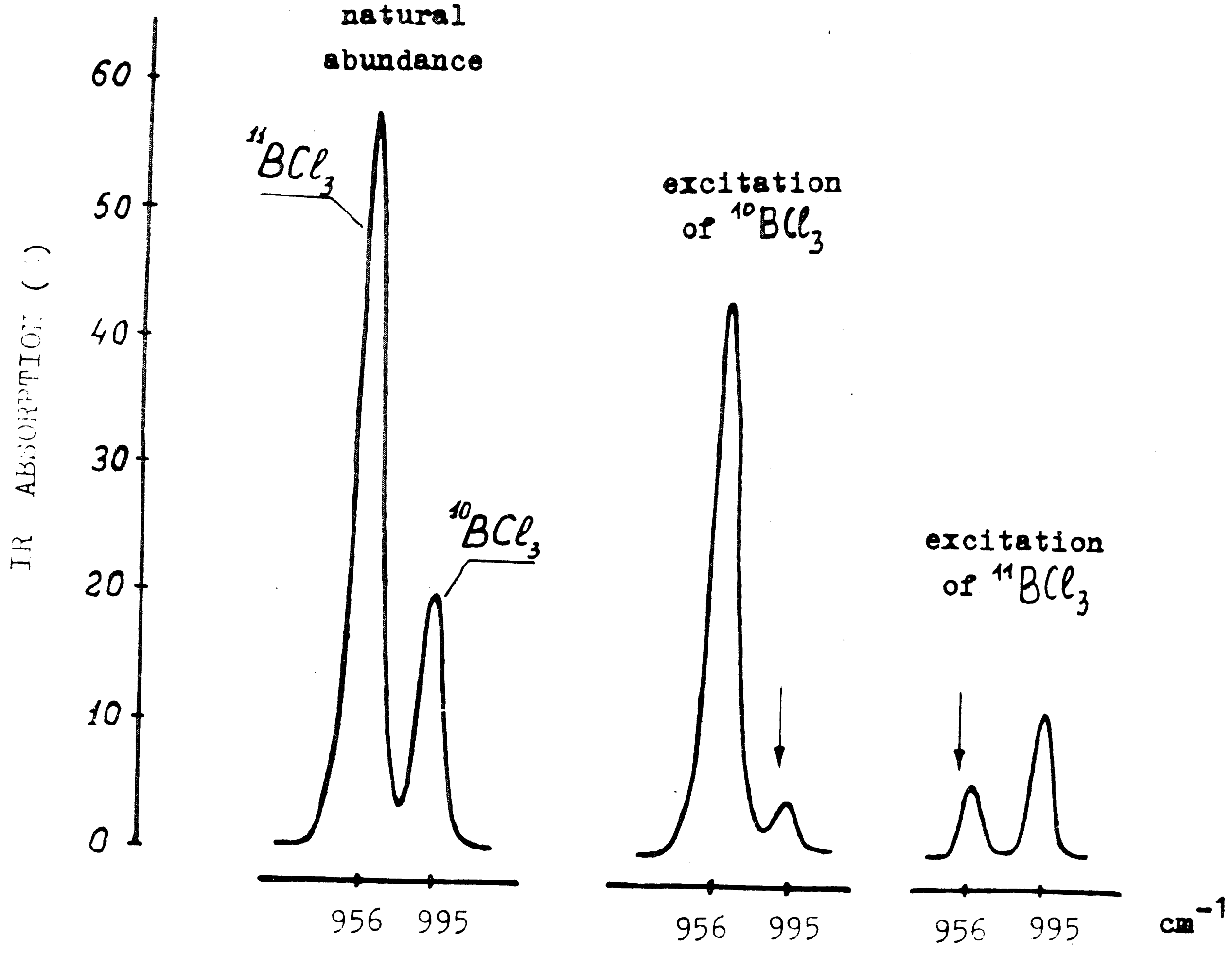
XBL 763-857

Fig. 1. Excitation scheme of molecular gas (BCl_3) fluorescence with a focussed pulse of CO_2 TEA laser: A - fluorescence from the focal region; B - fluorescence from the off-focal (shaded) region.



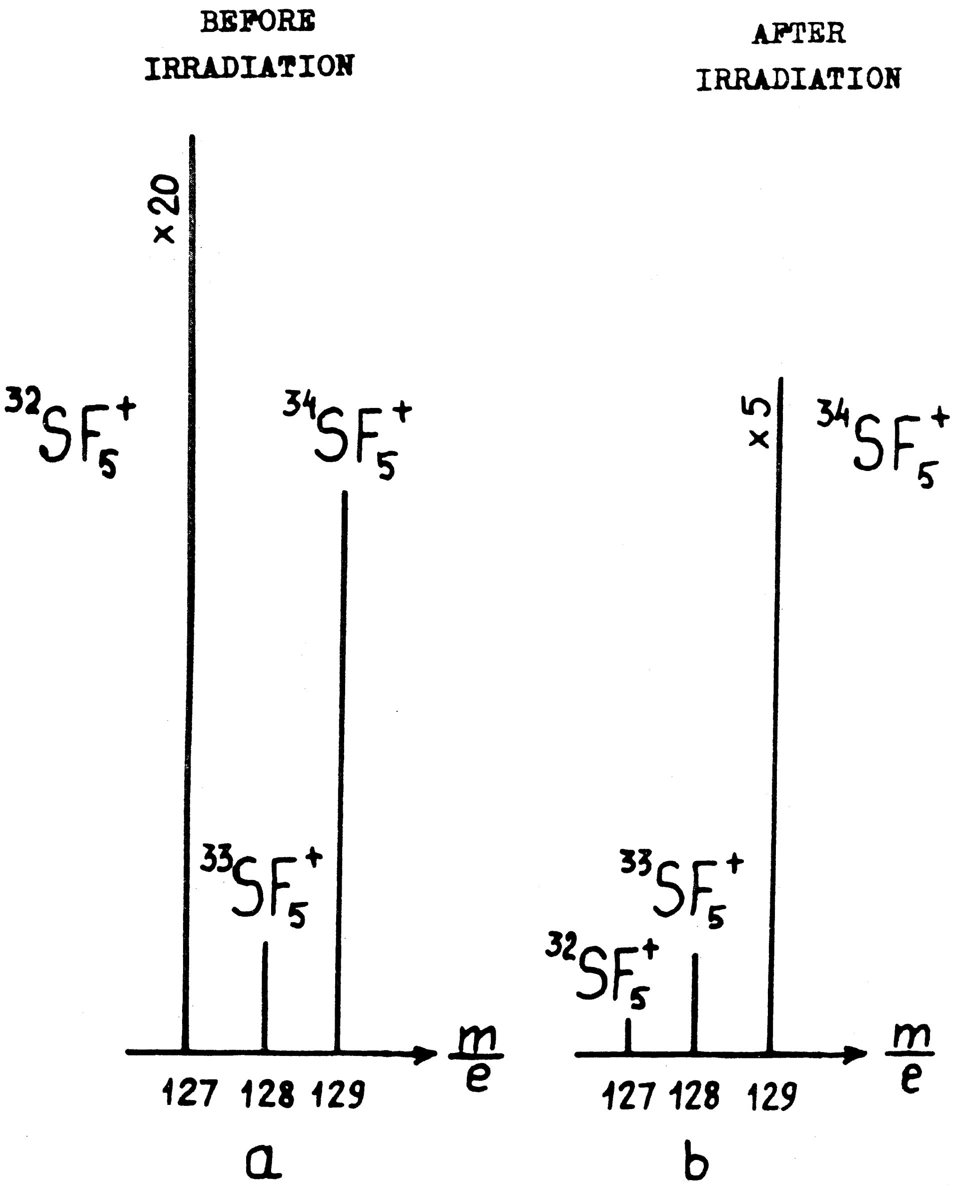
XBL 763-858

Fig. 2. Emission spectrum of BO at the transition (0,2) of the band $^2\Pi \rightarrow {}^2\Sigma$ during excitation of $^{10}BCl_3$ and $^{11}BCl_3$. At top the sections of emission spectra of ^{10}BO (dashed line) are given schematically (from work /1/).



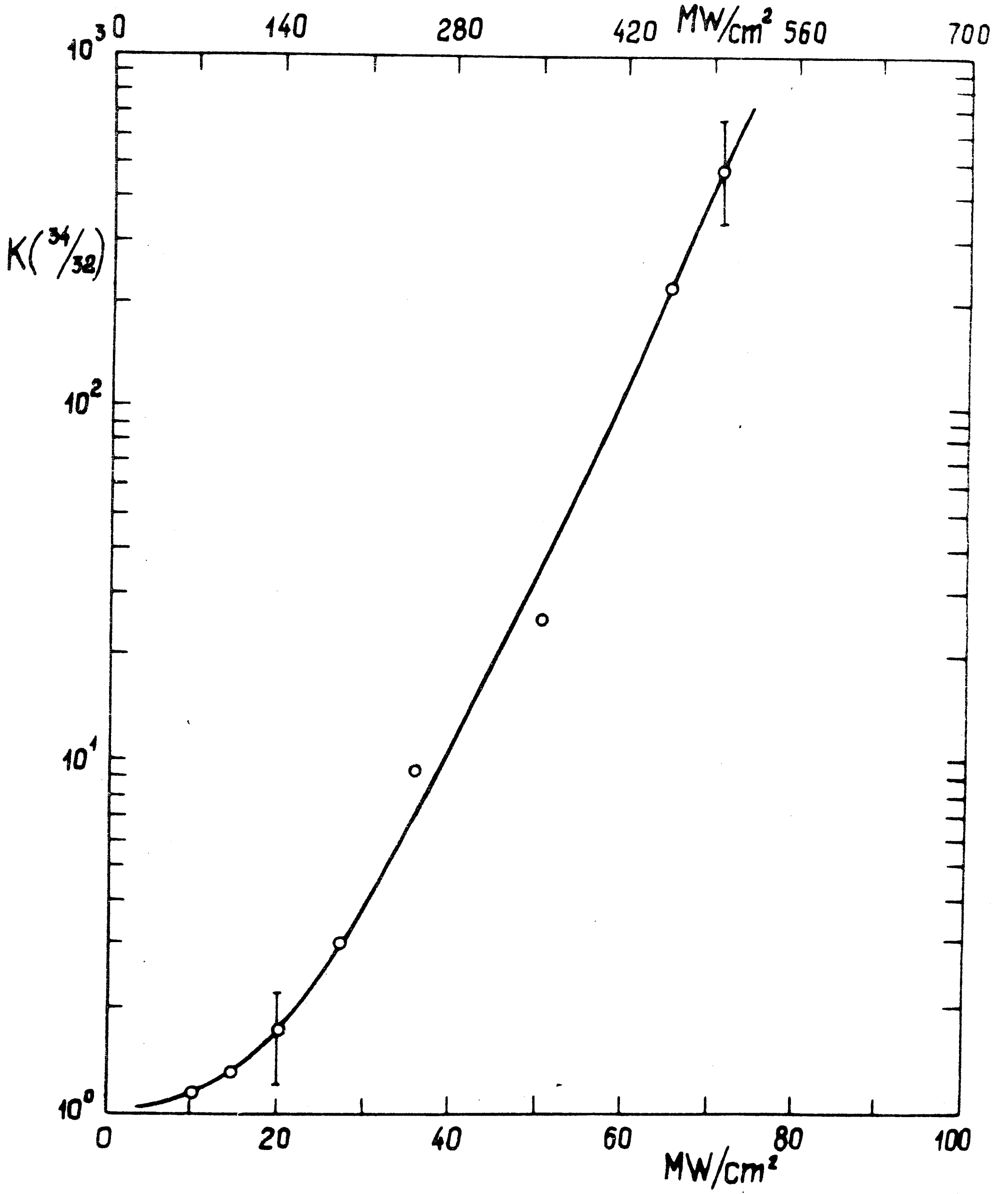
XBL 763-859

Fig. 3. IR absorption spectrum for the band ν_3 of the isotopic natural mixture of BCl_3 molecules: a) the isotopic mixture before irradiation; b) after irradiation at the absorption frequency of $^{10}BCl_3$; c) after irradiation at the absorption frequency of $^{11}BCl_3$. Mixture composition: BCl_3 - 0.44 Torr, air - 11Torr (work /9/).



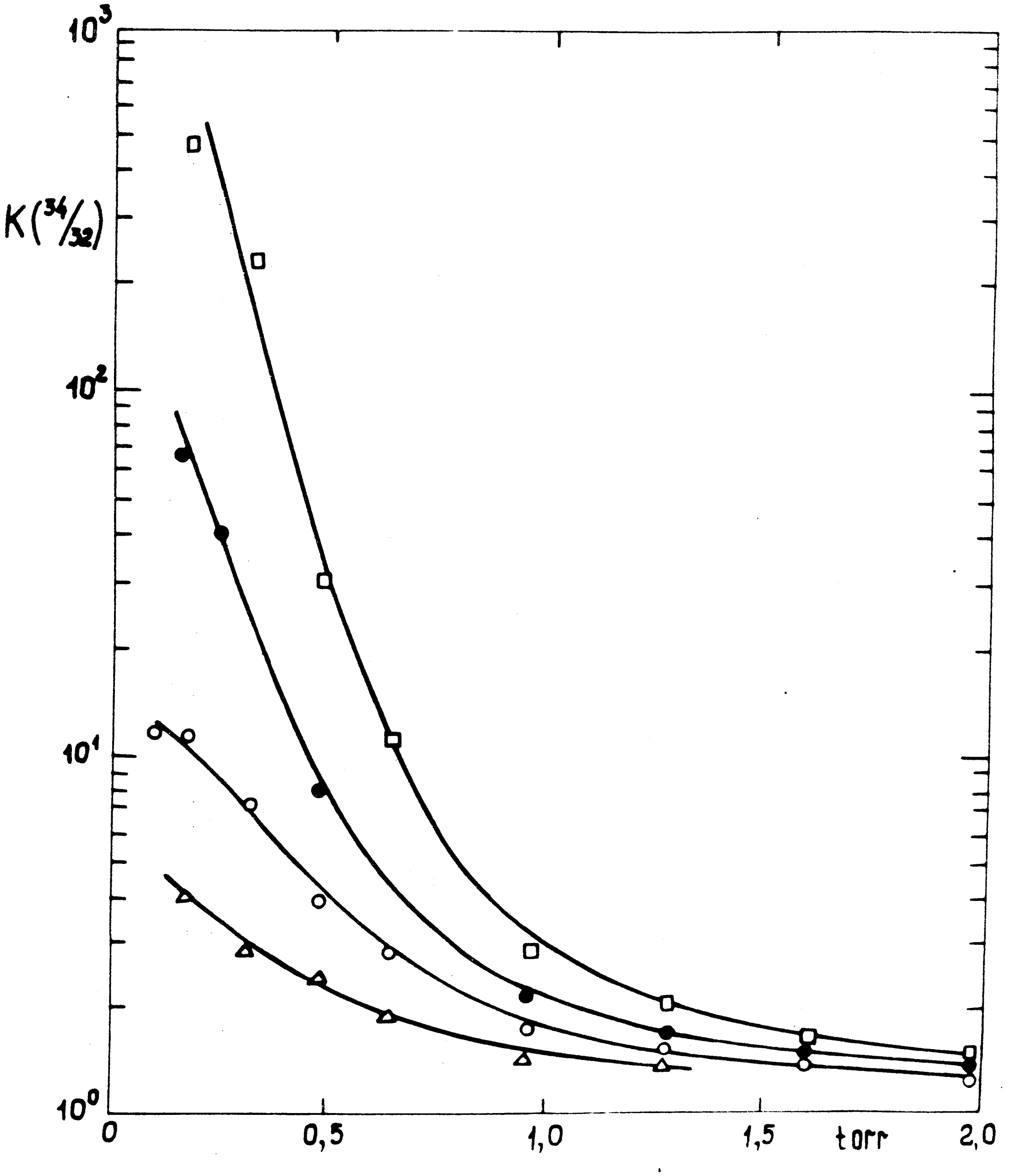
XBL 763-860

Fig. 4. A part of the mass spectrum of SF_6 (ionic fragment SF_5^+): a) the natural mixture before irradiation; b) after irradiation with $2 \cdot 10^3$ pulses of CO_2 laser at the line P(16) (from work /2/).



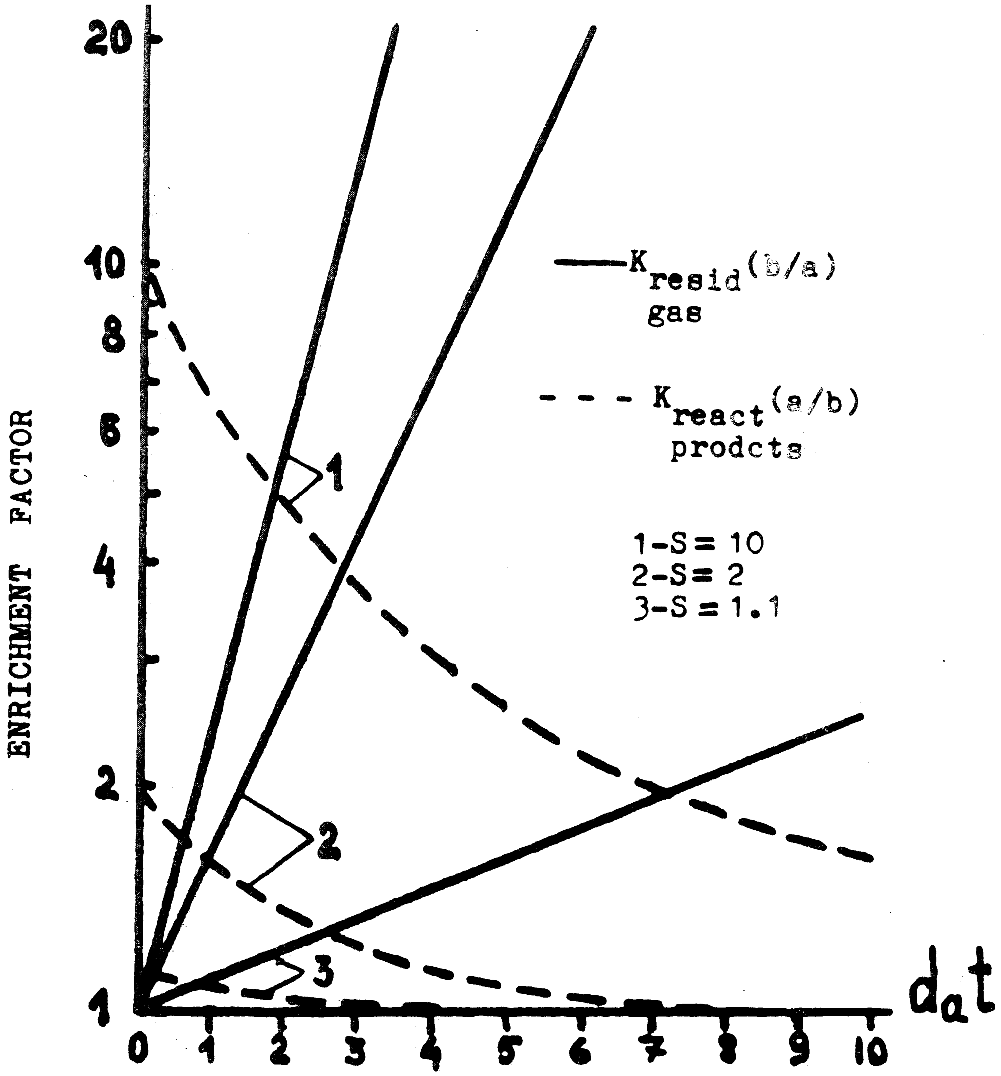
XBL 763-861

Fig. 5. Dependence of the enrichment coefficient K ($^{34}S/^{32}S$) on radiation intensity (the upper scale - the intensity in the focus, the lower scale - the average intensity in the region under irradiation). The pressure of SF_6 is 0.32 Torr, the number of irradiation pulses is 450 (from work /10/).



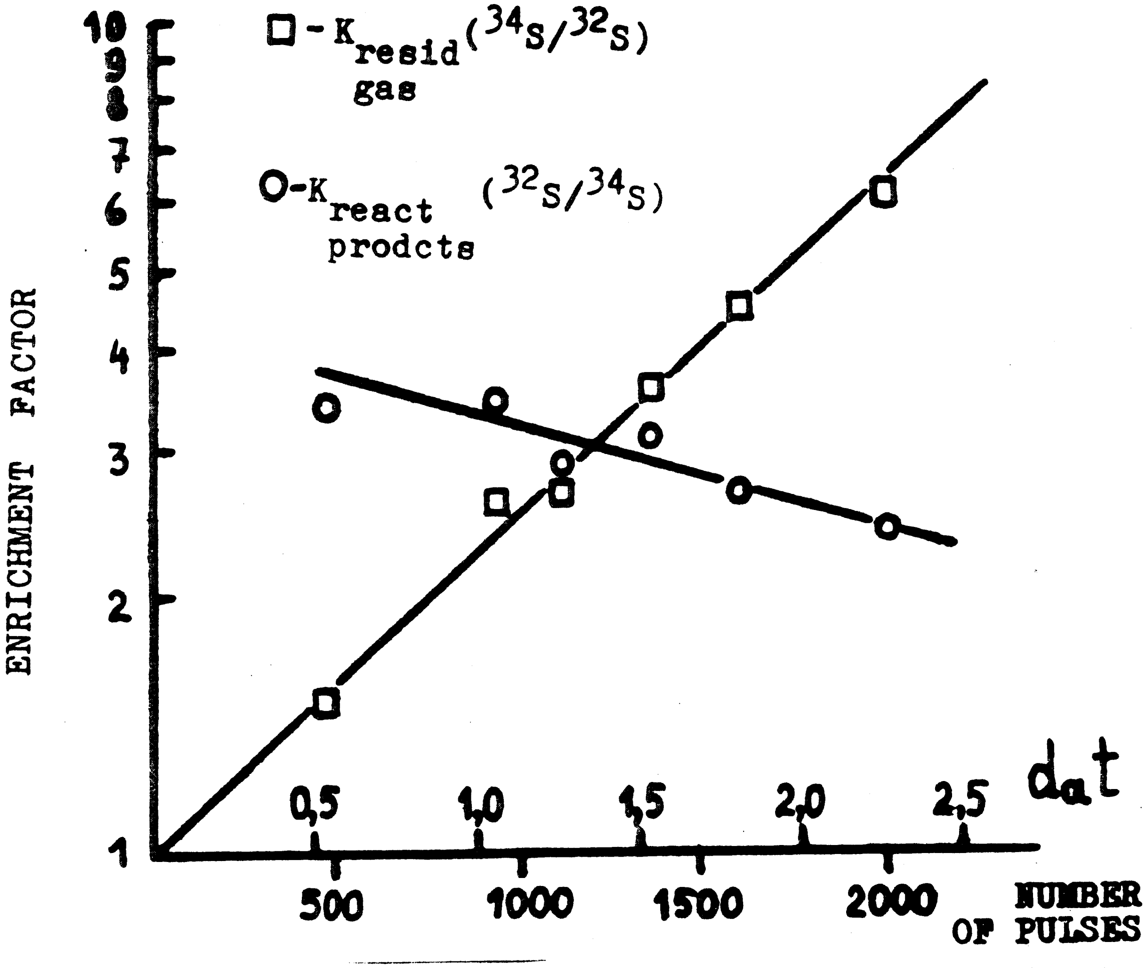
XBL 763-862

Fig. 6. Dependence of the enrichment coefficient $K(^{34}S/^{32}S)$ of residual SF_6 gas on the initial pressure of SF_6. The number of irradiation pulses is: △ - 50, ○ - 100, ● - 200, □ - 40 (from work /10/).



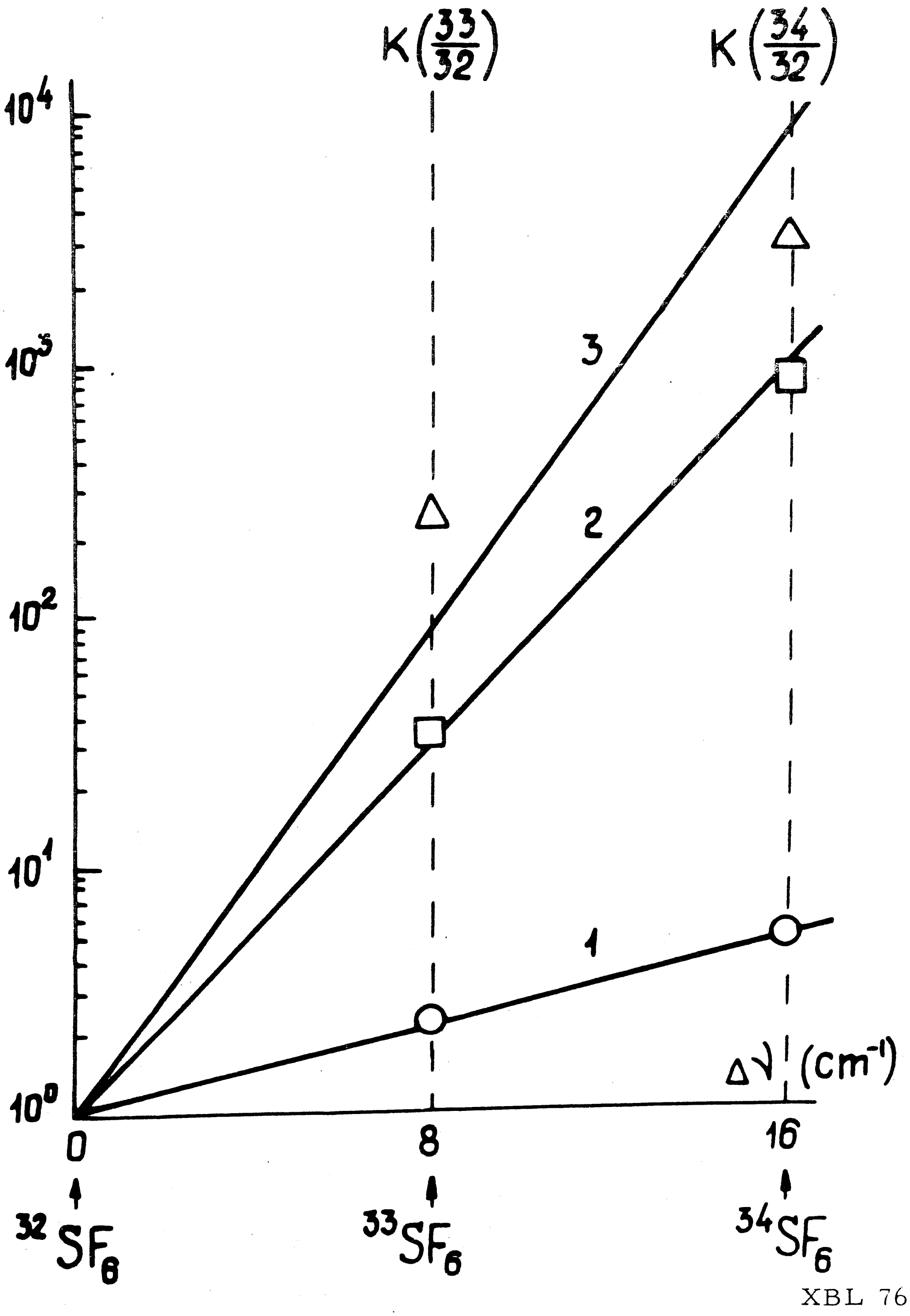
XBL 763-863

Fig. 7. Calculated dependences of the enrichment coefficient of residual gas K_{resid} (b/a) (solid curves) and of product molecules K_{prod} (a/b) (dashed curves) on time (or the number of pulses) during selective dissociation of "a" molecules in a two-component mixture with different values for the dissociation selectivity coefficient S (from work /10/).



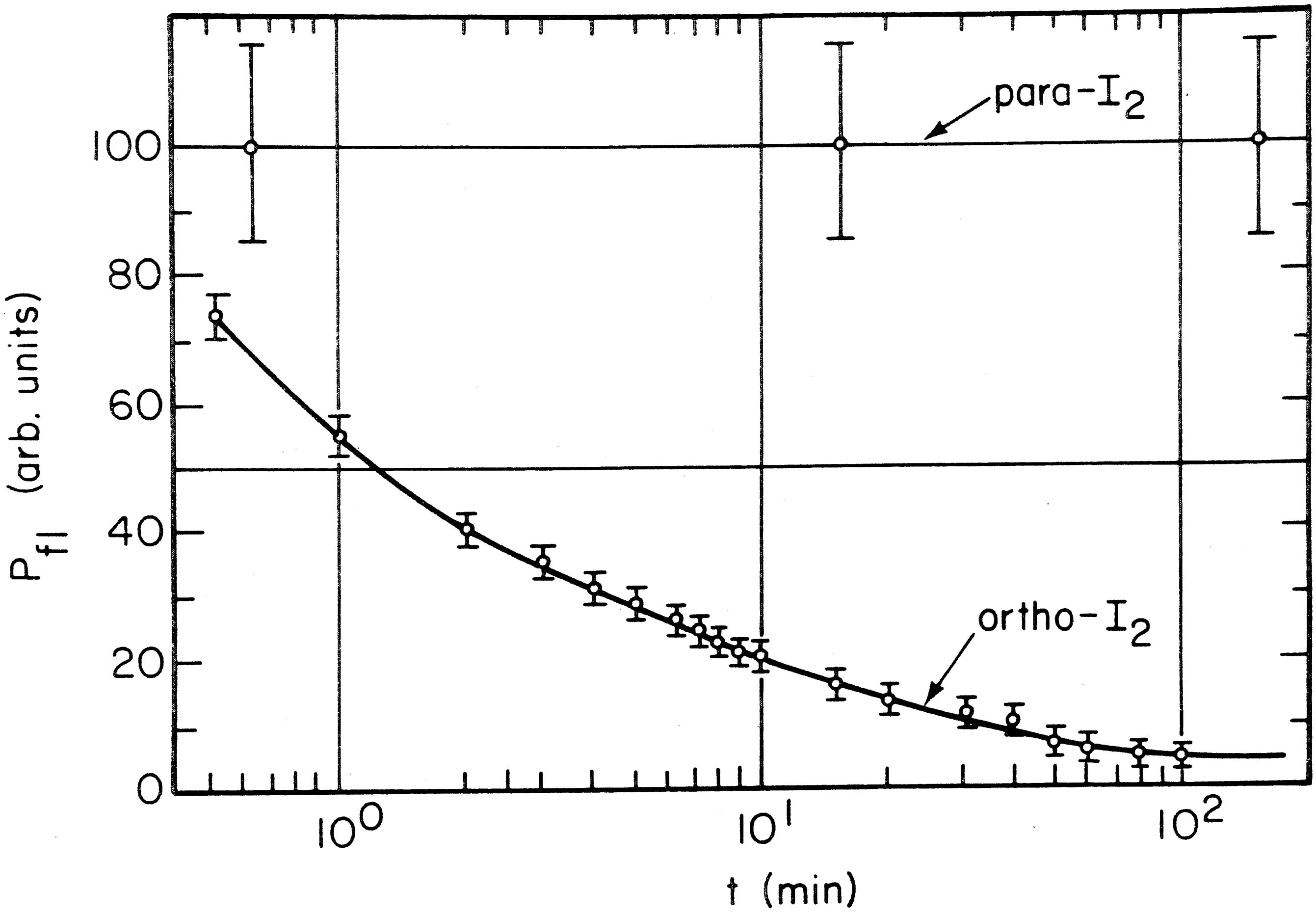
XBL 763-864

Fig. 8. Experimental dependence of the enrichment coefficient of residual gas K_{resid} and product molecules K_{prod} on the number of irradiation pulses during dissociation of $^{32}SF_6$ molecules in the natural mixture with the initial pressure of 1.6 Torr (from work /10/).



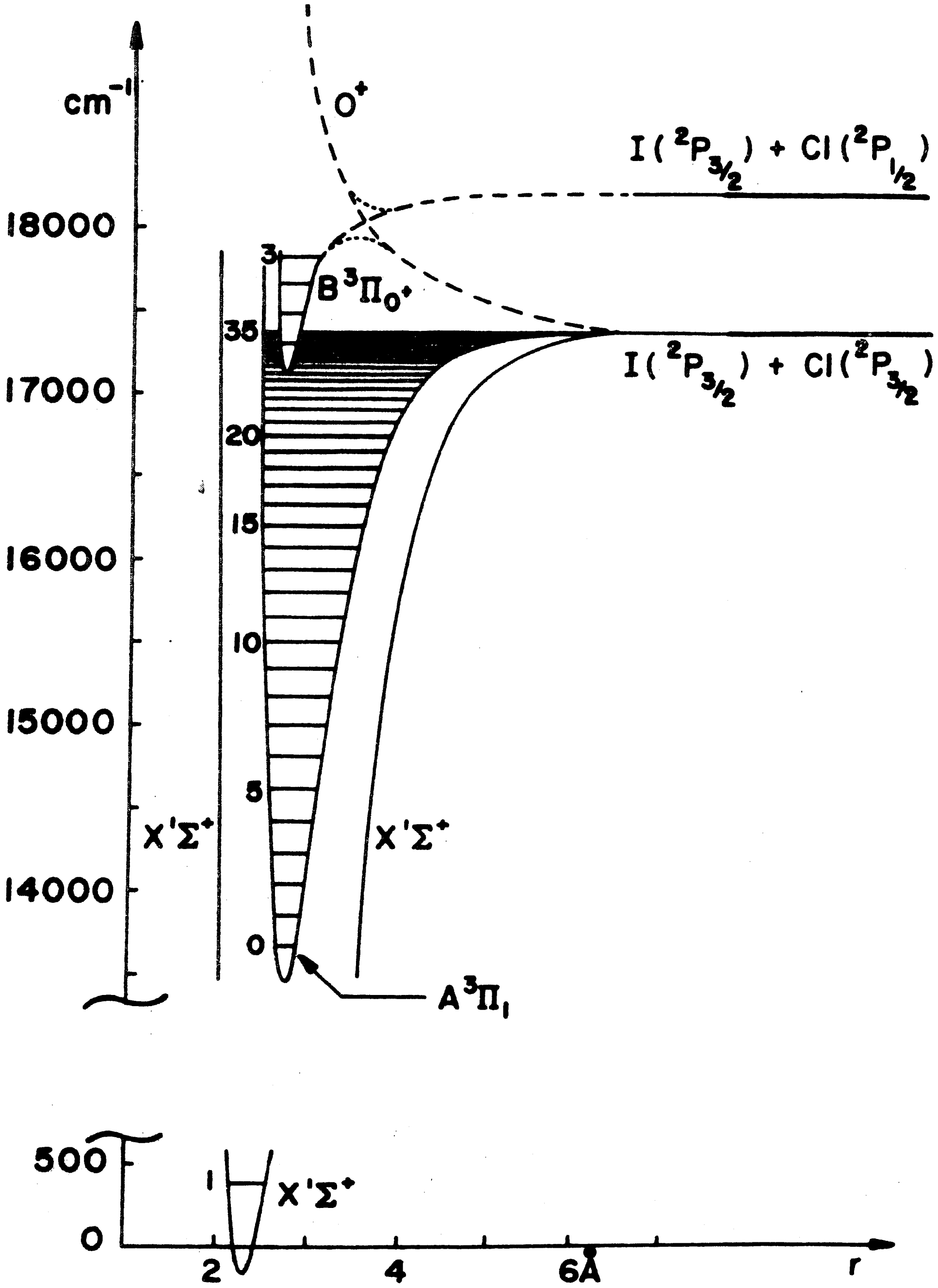
XBL 763-865

Fig. 9. Dependence of the enrichment coefficient on the isotope shift value for a laser-excited vibration. The pressure in the cell: 0.18 Torr of SF_6 + 2 Torr of H_2. Irradiation: 1 - 100 pulses, line P(12); 2 -400 pulses, line P(12); 3 - 2000 pulses, line P(16) (from work /10/).



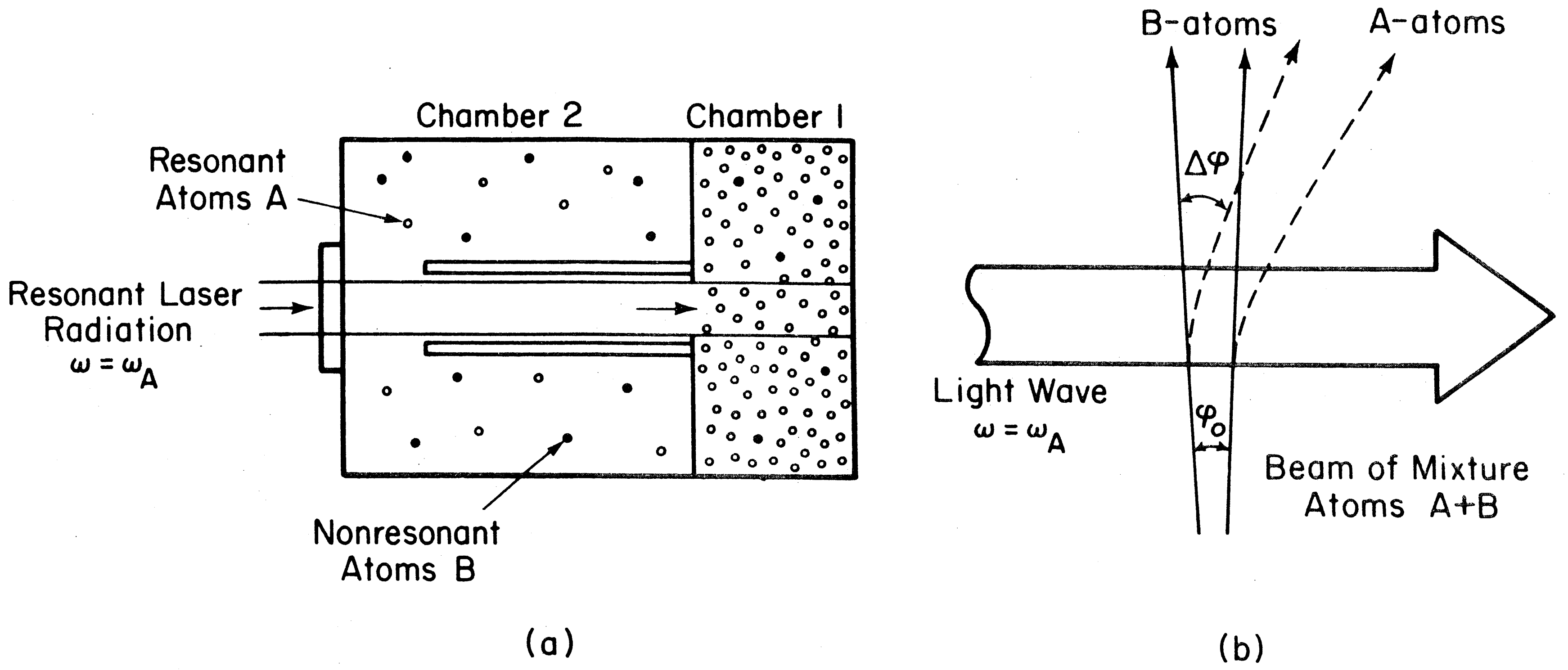
XBL 763-866

Fig. 10. Time dependence of ortho-I_2 fluorescence excited by the intense line 514.5 nm and of para-I_2 excited by the weak probe line 501.7 nm an argon laser (from work /37/).



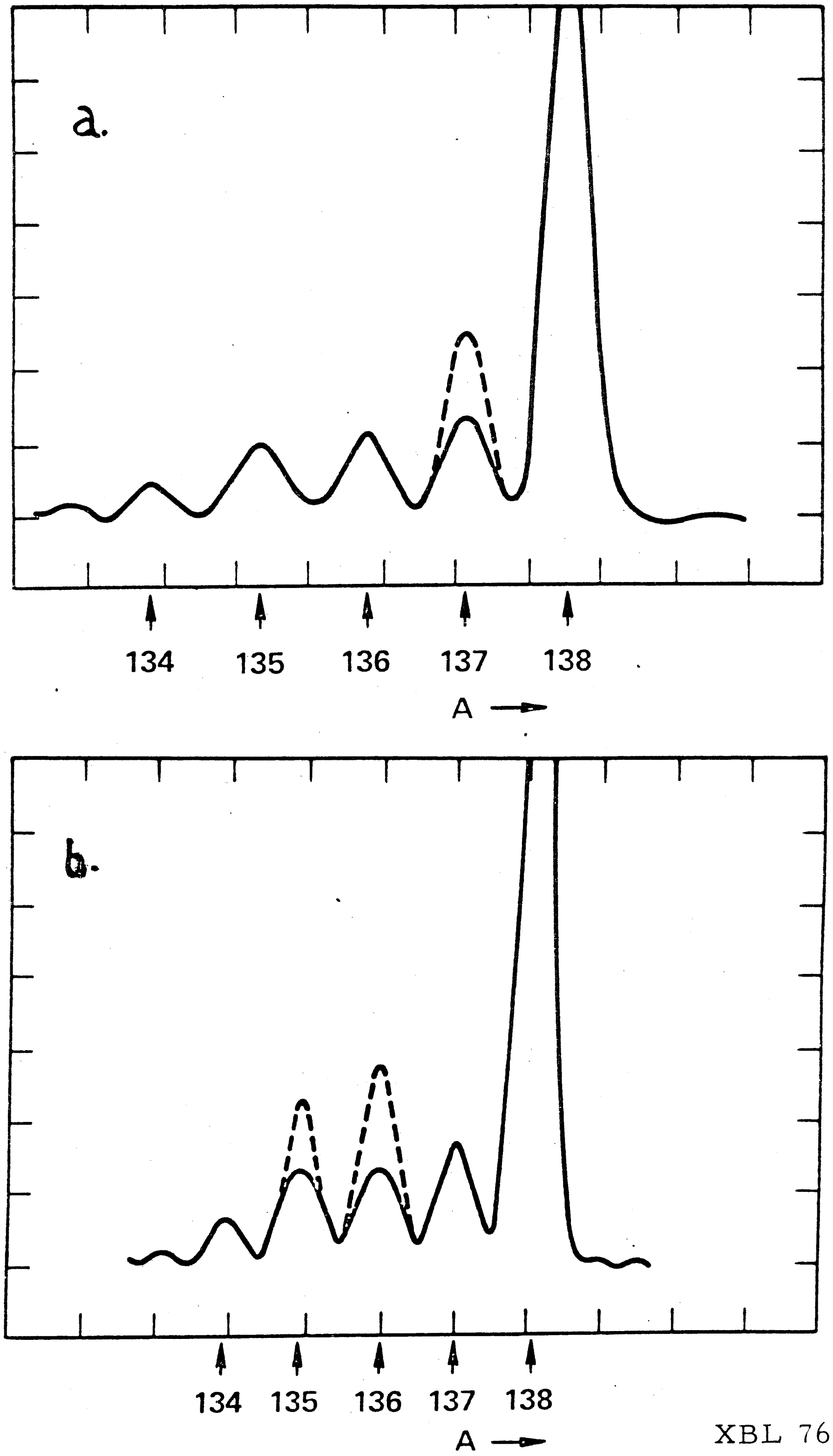
XBL 763-867

Fig. 11. Scheme of lower potential curves of ICl molecules (from work /41/).



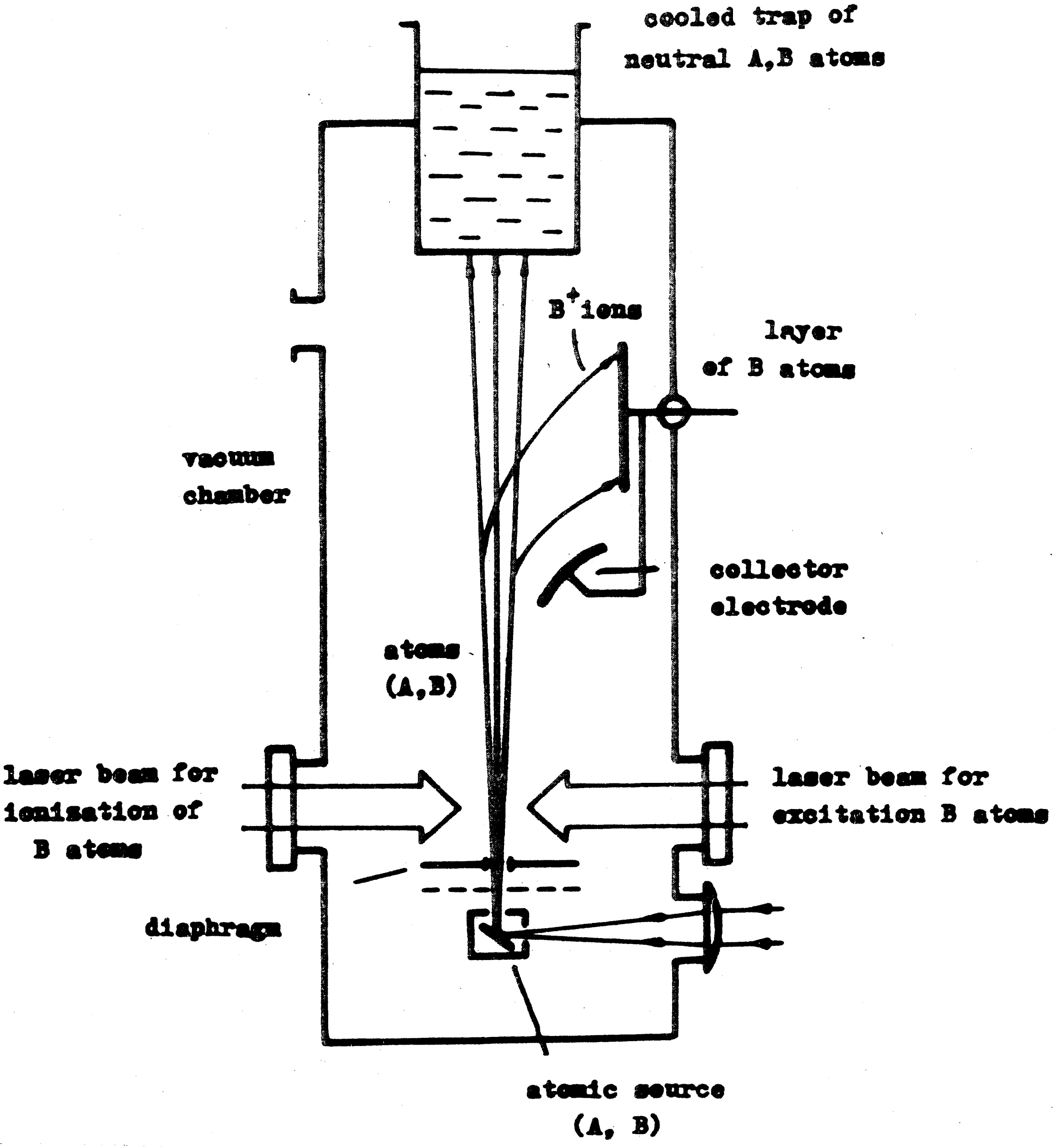
XBL 763-868

Fig. 12. **Isotope separation by selective light pressure: a particle mixture is acted upon in a gas (a) and in a beam (b).**



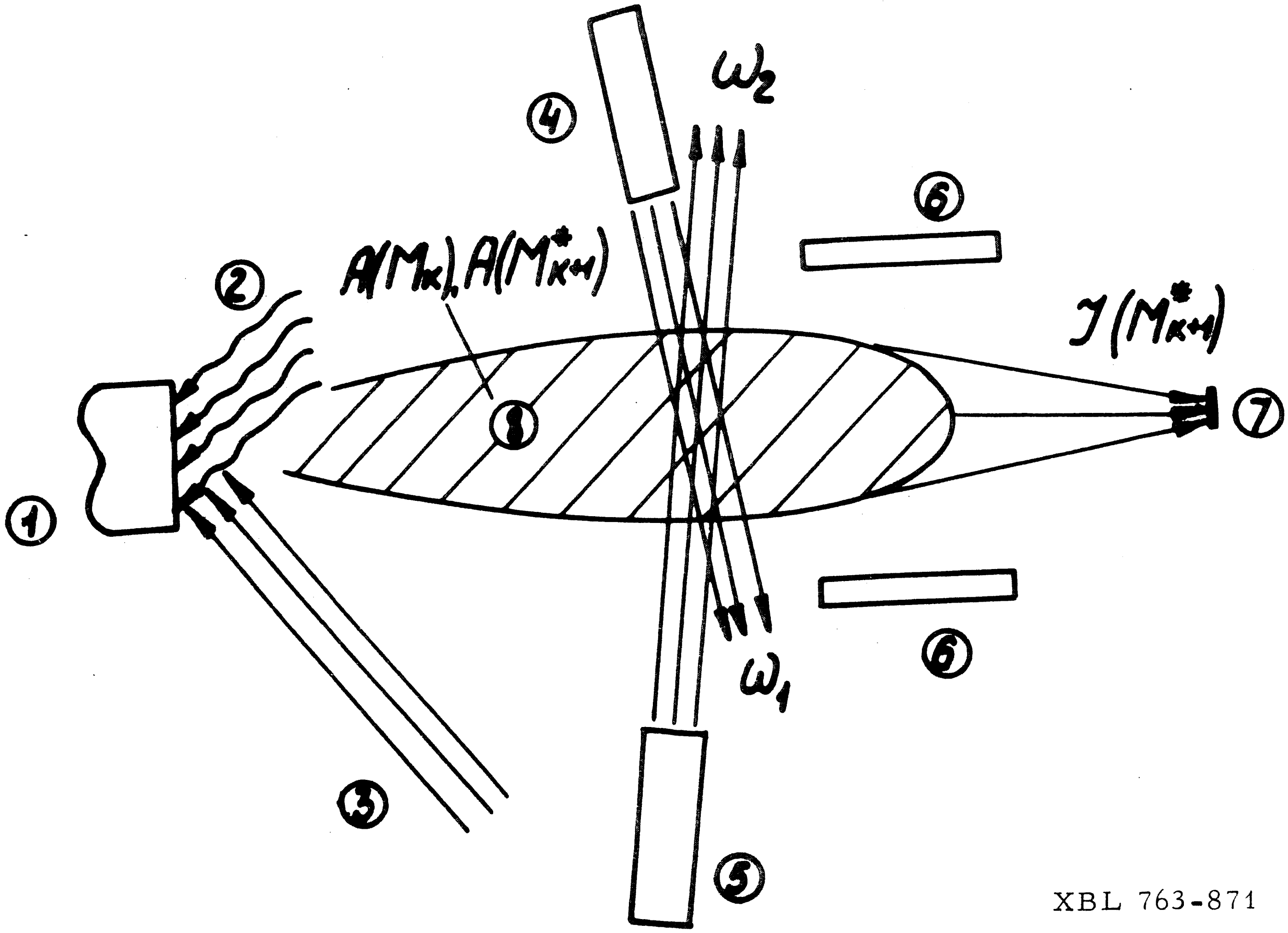
XBL 763-869

Fig. 13. The mass spectrum of the natural mixture of Ba isotopes (solid lines) and photodeflected Ba atoms (dashed lines) during resonant action of laser radiation on the hyperfine structure components of the ^{137}Ba isotope (a) and ^{135}Ba and ^{136}Ba atoms (b) (from work /92/).



XBL 763-870

Fig. 14. Possible scheme for preparation of films of highly pure composition during sedimentation of B^+ ions produced by the method of two-step selective ionization of atoms of the B sort in a beam when mixed with other atoms.



XBL 763-871

Fig. 15. **Possible scheme of a γ- laser on high-rate decay nuclear isomers employing laser sorting of excited nuclei** M_{k+1}: 1 - target of M_k atoms; 2 - beam of slow neutrons; 3 - laser beam for evaporation of surface layer of target; 4 - laser beam for excitation of $A(M^*_{k+1})$ atoms; 5 - laser beam for ionization of excited atoms $A(M^*_{k+1})$; 6 - collecting system; 7 - filament of atoms with excited nuclei M^*_{k+1}; 8 - stream of evaporated atoms. (from work /114/).