

Applied laser spectroscopy—Techniques and trends

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Modern research in atomic and molecular spectroscopy is mainly based on applications of lasers as spectroscopic sources. This has led to revolutionary advances, not only in fundamental spectroscopy studies, but also in techniques of applied spectroscopy in a variety of fields like analytical spectroscopy, atomic and molecular physics, chemical dynamics, surface studies, plasma physics, cosmology, biophysics and so on. In this article some of the applied aspects of laser spectroscopy are presented. Areas like laser-enhanced ionization spectroscopy, resonance multiphoton ionization, spectroscopy of discharges and flames, supersonic beams, and laser-ablated metal vapour spectroscopy are illustrated with reference to the current techniques and future trends.

Modern spectroscopy, especially with reference to basic studies for determination of molecular constants, energy levels, vibration-rotation interactions, hyperfine and superfine structures, absorption, ionization and dissociation cross-sections, etc., has made tremendous advances in recent years. The application of highly refined laser techniques¹ like saturation and polarization spectroscopy, optical-optical and optical-microwave double resonance, side-band generation, and doppler-free multiphoton transitions has improved temporal, spatial and energy resolution by several orders of magnitude compared to resolutions available till recently. The use of lasers has led to equally revolutionary advances in various fields of applied spectroscopy, also resulting in the use of spectroscopy techniques for advanced research in almost all branches of science. Techniques developed and refined for basic studies in spectroscopy are now being applied in several areas of research to obtain information that could not be obtained otherwise. An idea of the variety of applications of laser spectroscopy can be seen from Figure 1, which shows schematically many of the areas where unique information has been obtained through laser spectroscopy. In this article, I discuss some of these areas in which my laboratory has been involved in the past few years.

Ultra-trace analysis

Ultra-trace analysis has become extremely important in several areas like medicine, nuclear energy programmes, cosmology, geochronology, and environmental applica-

tions. For example, there are several elements, called 'essential elements', that were considered to be toxic earlier but are now known to be important when present in ultra-trace levels in body fluids. Cr, Cu, Se, Sr, Zn and Ni are examples. There are other elements like Cd, Hg and Pb, which, when present in extremely small amounts, do not pose any problems, but at slightly higher concentrations become highly toxic. The concentration range where analyses for these elements have to be done is thus in the trace and ultra-trace levels.

Ultra-trace analyses are required in many areas of nuclear programmes like fuel processing, waste disposal, environmental contamination, and internal dosimetry. There are several challenging problems in nuclear physics (e.g. double β -decay of ^{136}Xe , nuclear properties of short-lived isotopes and isomers), geochronology (determination of ^{81}Kr and other rare-gas isotopes), cosmology (analysis of Tc for solar neutrino flux), etc. that can be solved by ultra-trace analysis, at the parts-per-billion (ppb) and parts-per-trillion (ppt) levels.

Till recently, analyses at these levels were often beset with problems of contamination, inaccuracy and low sensitivity. The very high sensitivity achievable with

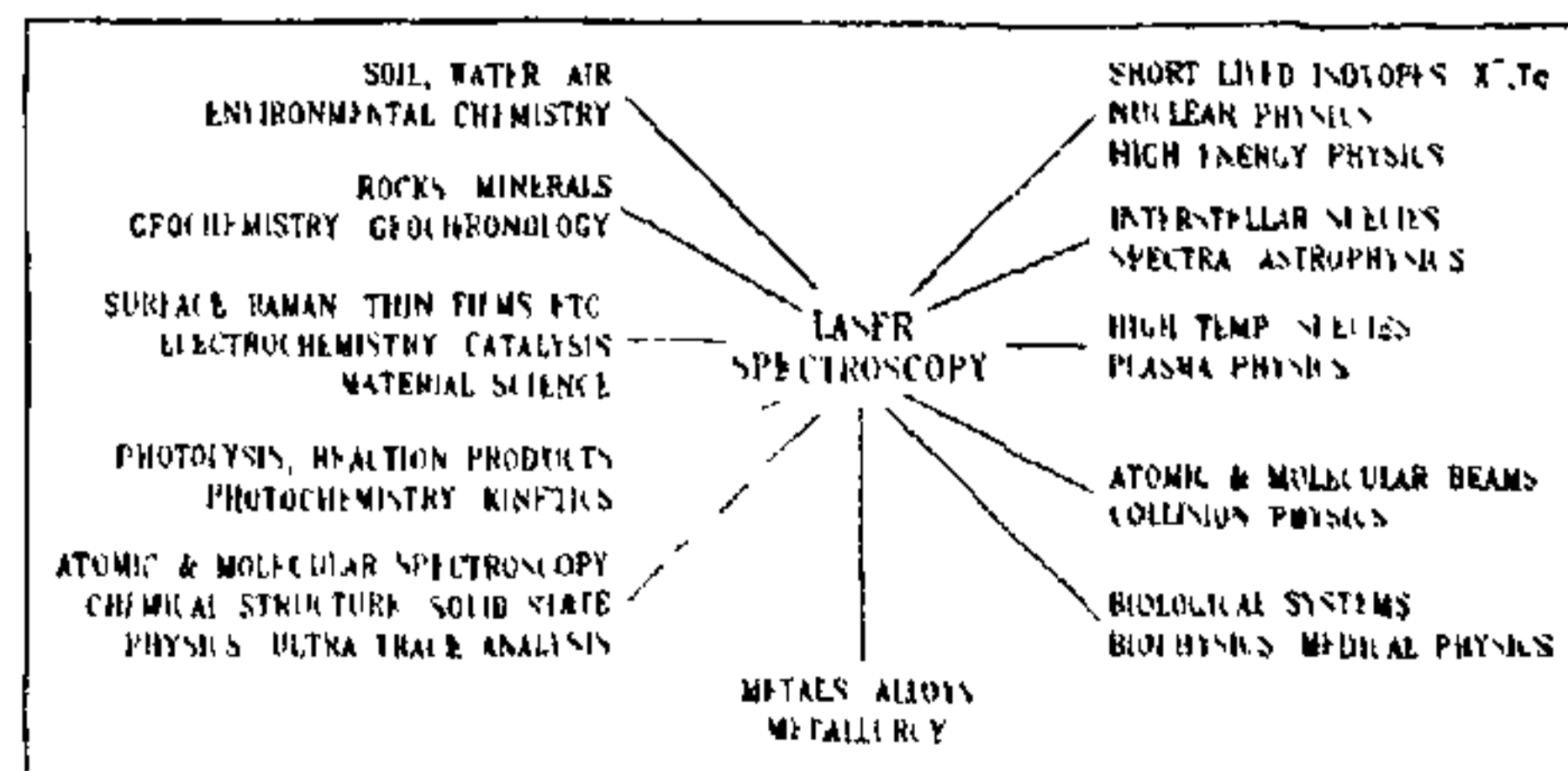


Figure 1. Laser spectroscopy - areas of application

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laser techniques has made analyses possible without preconcentration in many cases, thus reducing contamination problems. Accuracy also has improved by the use of more stabilized lasers, multistep excitation to eliminate interferences, and minimum sample handling and processing achieved by direct analysis in many cases.

Laser-induced fluorescence (LIF), laser resonance ionization, laser optogalvanic spectroscopy, and photo-thermal and photoacoustic spectroscopy are some of the techniques²⁻⁴ that are extremely effective for accurate determination of very small numbers of atoms or molecules, either when present alone or as an impurity in another material.

The use of LIF for ultra-trace analysis is now very well developed and number densities of the order of 10^3 ml^{-1} or less can be detected in favourable cases⁵⁻⁷. The technique has been used by us in several instances^{8,9} not only for analysis but also for spectroscopic studies. The experimental set-up and detection techniques for LIF are very well known and I will not discuss them further except to note that techniques like site-selection spectroscopy² have become very effective in ultra-trace analysis recently.

Laser-enhanced ionization (LEI) has become an established technique for ultra-trace analysis at present⁴. The technique involves the atomization of the sample in a flame or carbon-rod atomizer, as in atomic absorption, and exciting the atom of interest selectively using a high-power laser. The excited atoms are ionized (after further excitation, if necessary) by collisional processes. The ions produced are then collected and counted. The method is extremely sensitive, both because of the high sensitivity of charge detection and the fact that, at the temperature of the flame, the background ion number density is negligible, giving almost zero background signal.

A typical experimental set-up for LEI in flames is shown in Figure 2. Figure 3 shows the LEI spectrum

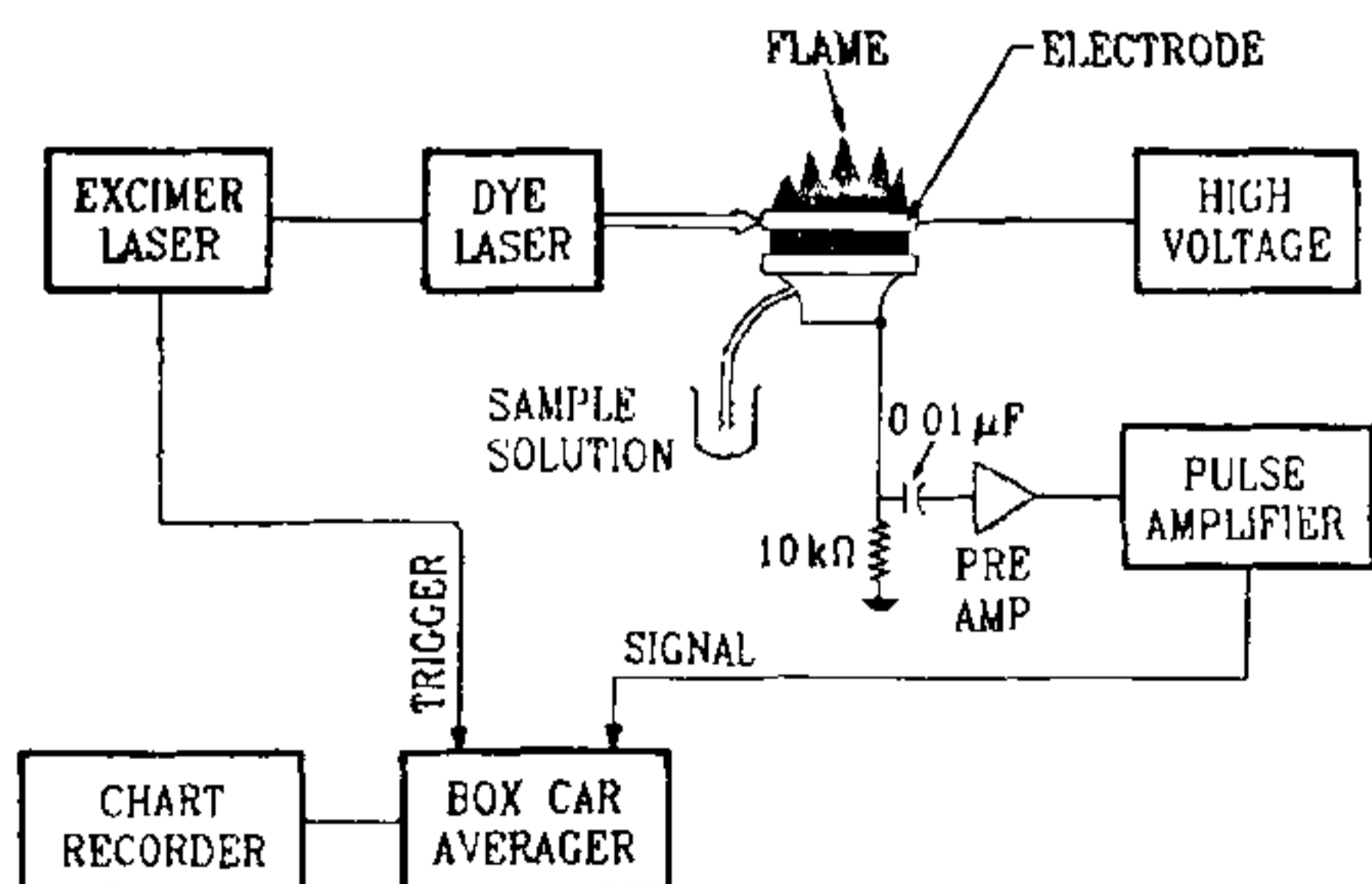


Figure 2. Block diagram of experimental set-up for laser-enhanced ionization (LEI) in flames

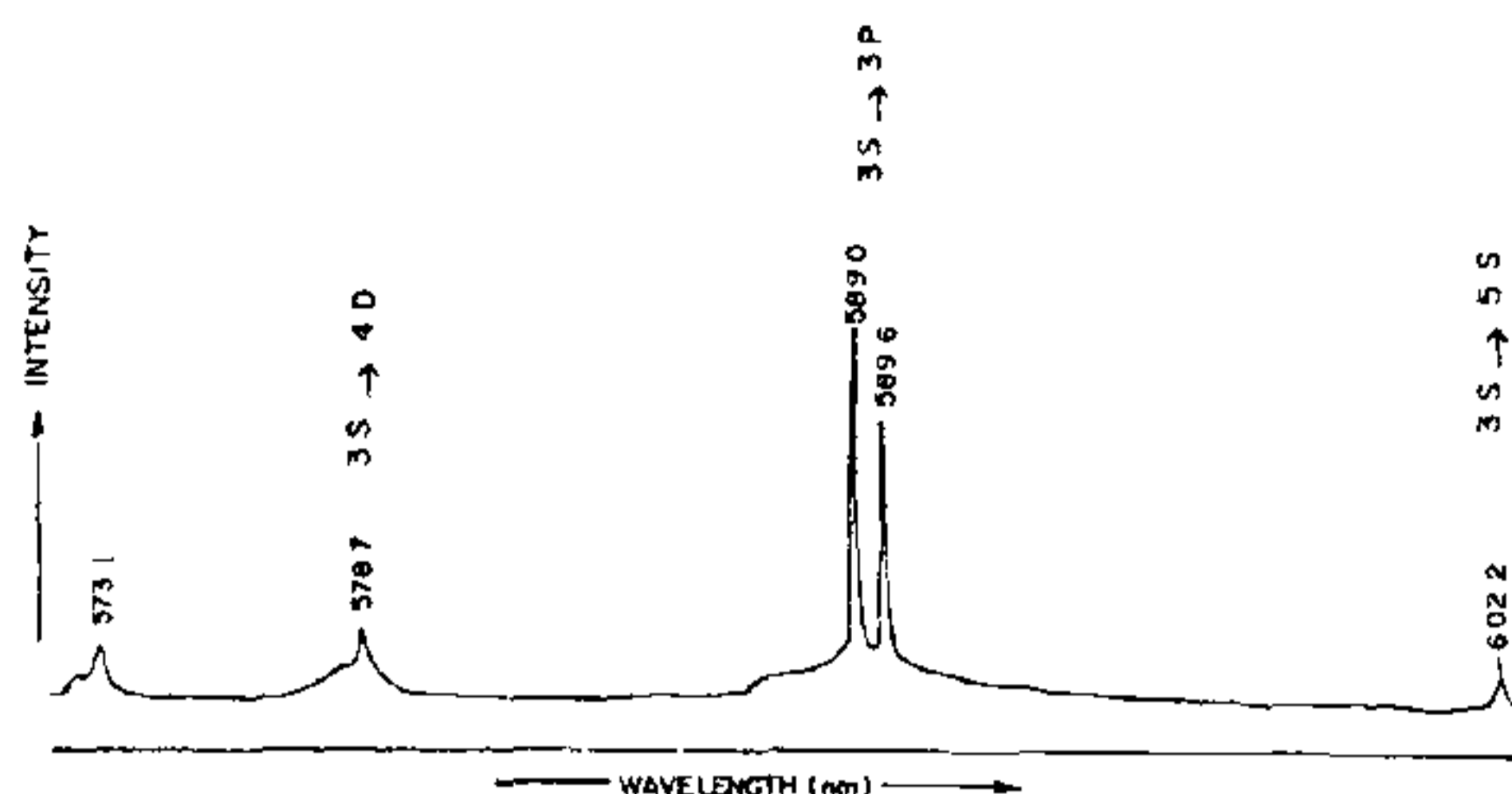


Figure 3. LEI spectrum of Na in flame excitation, excimer laser-pumped rhodamine 6G dye laser. Both single-photon ($3s \rightarrow 3p$) and two-photon ($3s \rightarrow 5s$ and $3s \rightarrow 4D$) transitions are observed

obtained with NaCl solution aspirated in the flame, in the region covered by rhodamine 6G dye¹⁰. From Figure 3 it can be seen that, in addition to the two lines at 589.0 and 589.6 nm corresponding to the *D* lines, there are two weak lines at 602.2 nm and 578.7 nm. These two lines correspond to the transitions $5s \leftarrow 3s$ and $4D \leftarrow 3s$, which are forbidden in single-photon absorption. At the high power used in the study, two-photon transitions take place with sufficient intensity so that these are observed without any difficulty. It should be noted that the one-photon transition takes the atom only to levels that are far below the ionization limit, while the two-photon transitions enable them to reach very near the ionization limit. As a result, while almost all the atoms excited in two-photon transitions will be ionized in subsequent collisions, many of the atoms excited to the lower level will be lost in collision following excitation. An interesting consequence of this is the possibility that the sensitivity for analysis may be more with two-photon transitions, in spite of the orders-of-magnitude lower cross-section for such processes. In the case of Na, this is indeed the case, as seen from Figure 4, where calibration curves obtained using both single-photon and two-photon transitions are shown for Na (ref. 11). The detection limit for the two-photon transition is much lower than that for the single-photon transition.

Laser multiphoton ionization (resonance-excited multiphoton ionization, REMPI), either alone or combined with mass spectrometry (RIMS), is now considered the most sensitive technique for detection and study of atomic or molecular species. The experimental set-up for this technique is more complicated than that for LEI, since it requires more than one tunable laser, for multistep excitation and ionization. An experimental system used in some of our studies is shown in Figure 5. Typical results obtained during a study of the spectrum of uranium are shown in Figure 6 (ref 12). These studies have been carried out with number densities of the order of 10^8 ml^{-1} , and even spectra

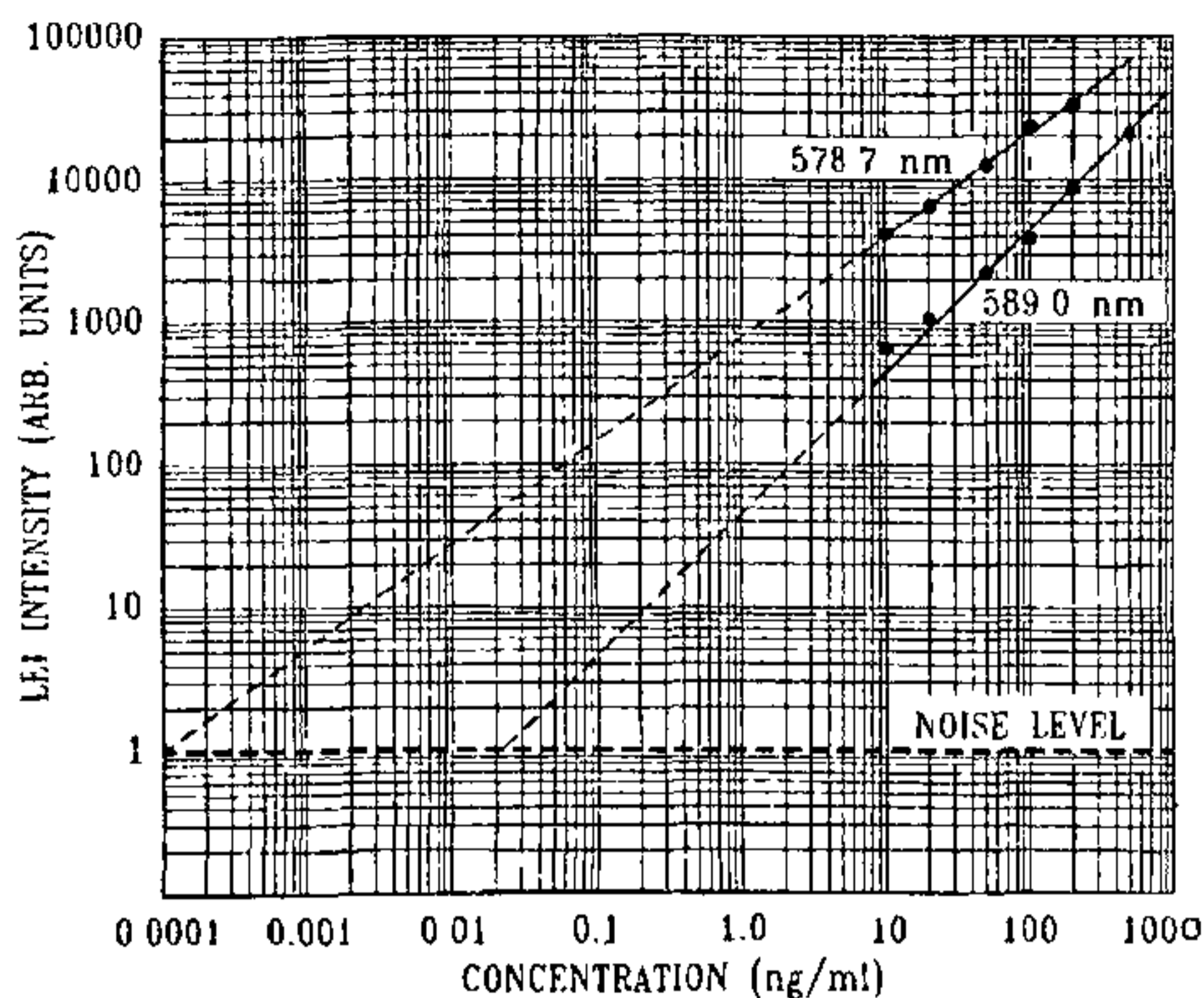


Figure 4. LEI calibration for Na. The 578.7-nm two-photon transition gives a better signal-to-noise ratio and detection limit compared to the single-photon transition at 589.0 nm.

arising from transitions from metastable levels, the populations of which are several orders of magnitude smaller than those in the ground state, have been obtained in these studies. The technique is now being

refined by various groups for fundamental studies in geochronology¹³, high-energy physics¹⁴, nuclear structure theory¹⁵, cosmology¹⁶, and so on.

Discharges and plasmas

The technique of LEI is related to a more general technique called laser optogalvanic (LOG) spectroscopy¹⁷, which depends on the detection of the change in impedance of a plasma by irradiation with a laser. Though there are several techniques like coherent anti-Stokes Raman spectroscopy (CARS)¹⁸, velocity modulation spectroscopy¹⁹ and magnetic field modulation²⁰ spectroscopy, LOG spectroscopy has several advantages over these techniques for the study of discharges and plasmas. It is applicable to atomic, molecular and ionic species, is highly sensitive, and can be adapted to ultra-high-resolution techniques like saturation spectroscopy and inter-modulated spectroscopy. Figure 7 shows an experimental set-up for LOG study of a refractory element, and Figure 8 shows the hyperfine structure of ²³⁵U observed with a natural uranium sample²¹ (0.7% ²³⁵U).

LOG spectroscopy can be used successfully in the study of dynamics of discharges and plasmas, to gain

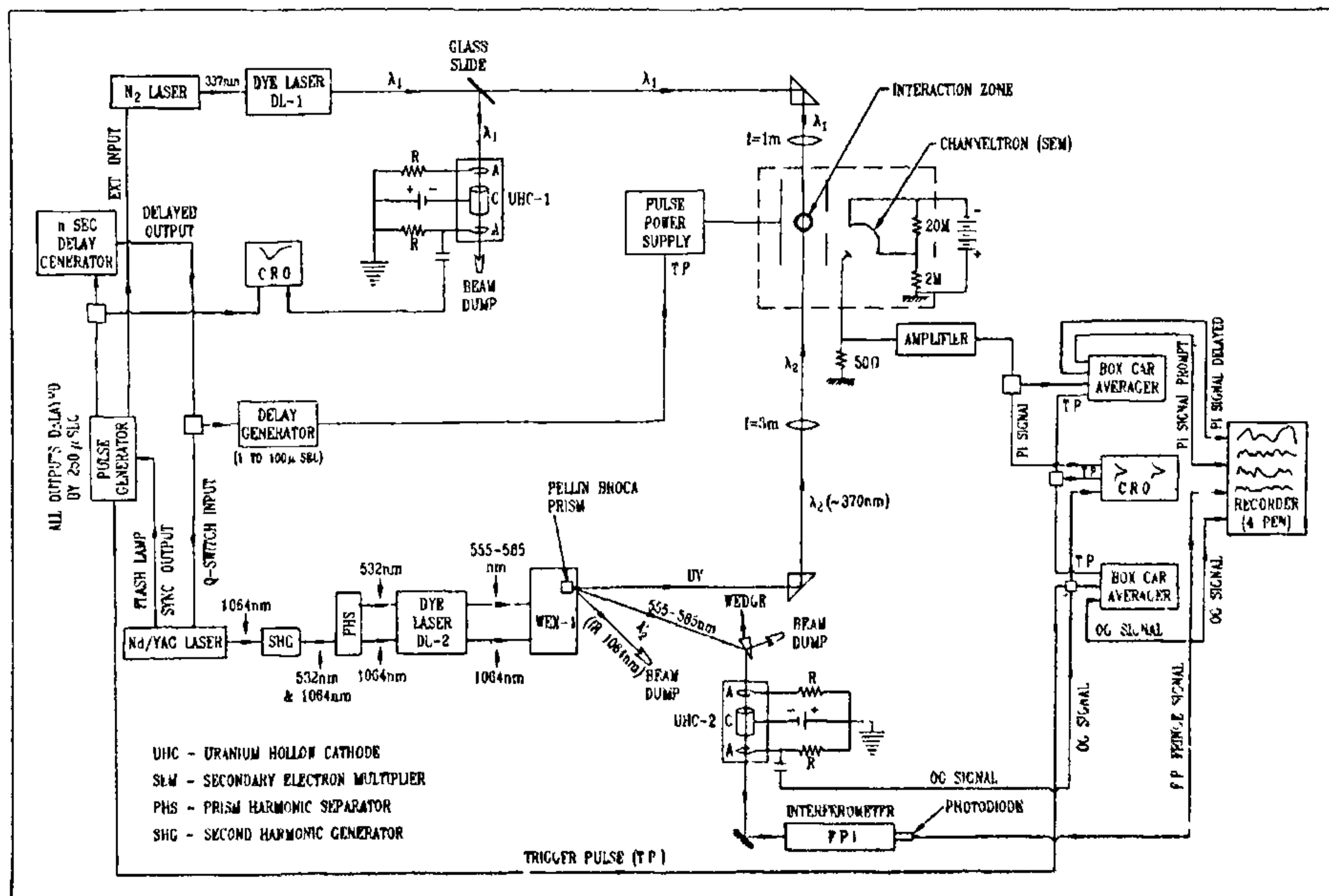


Figure 5. Experimental system for resonance-excited multiphoton ionization (REMPI).

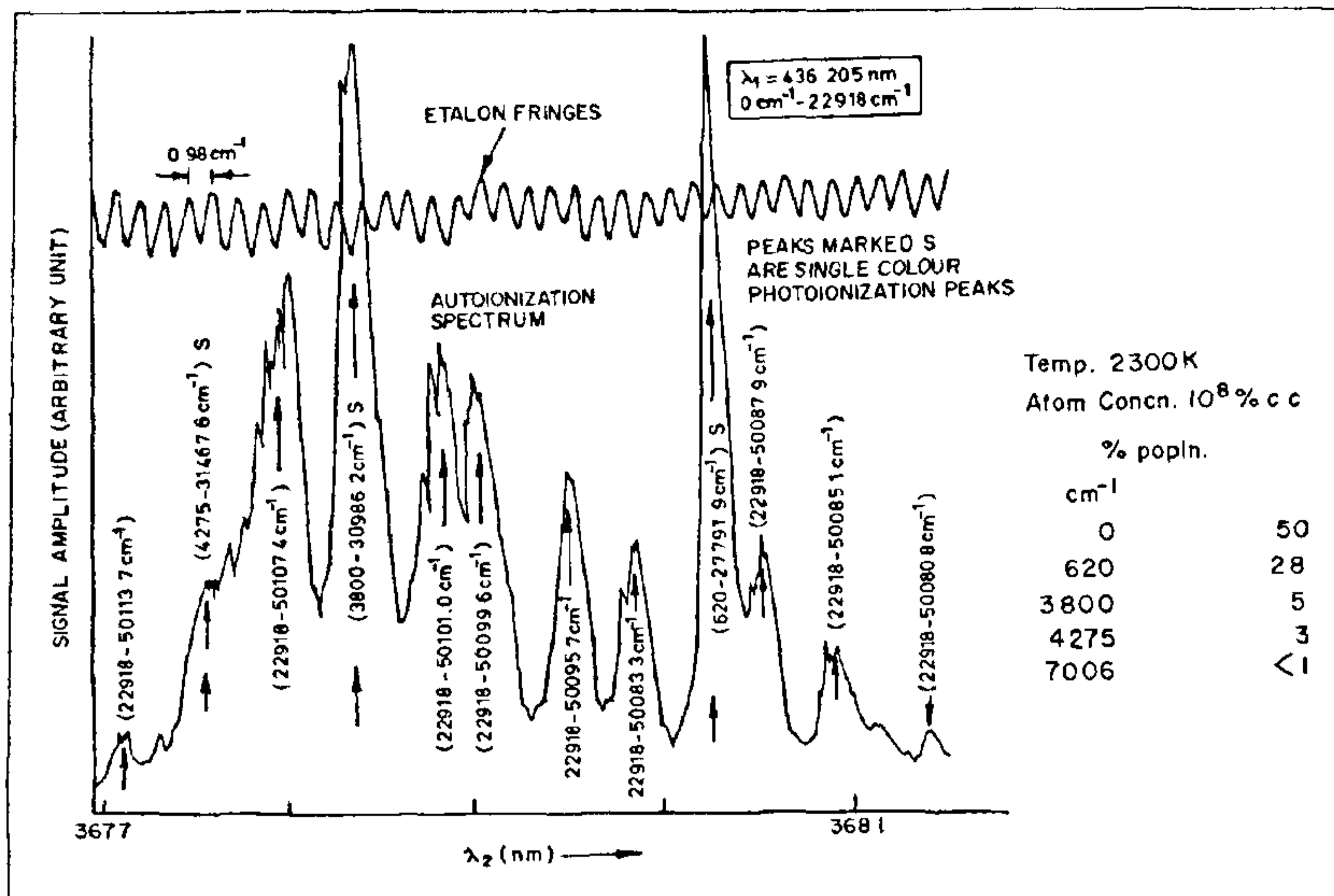


Figure 6. REMPI signals for uranium. The arrows indicate signals from metastable levels, with comparatively small population densities as shown in the figure

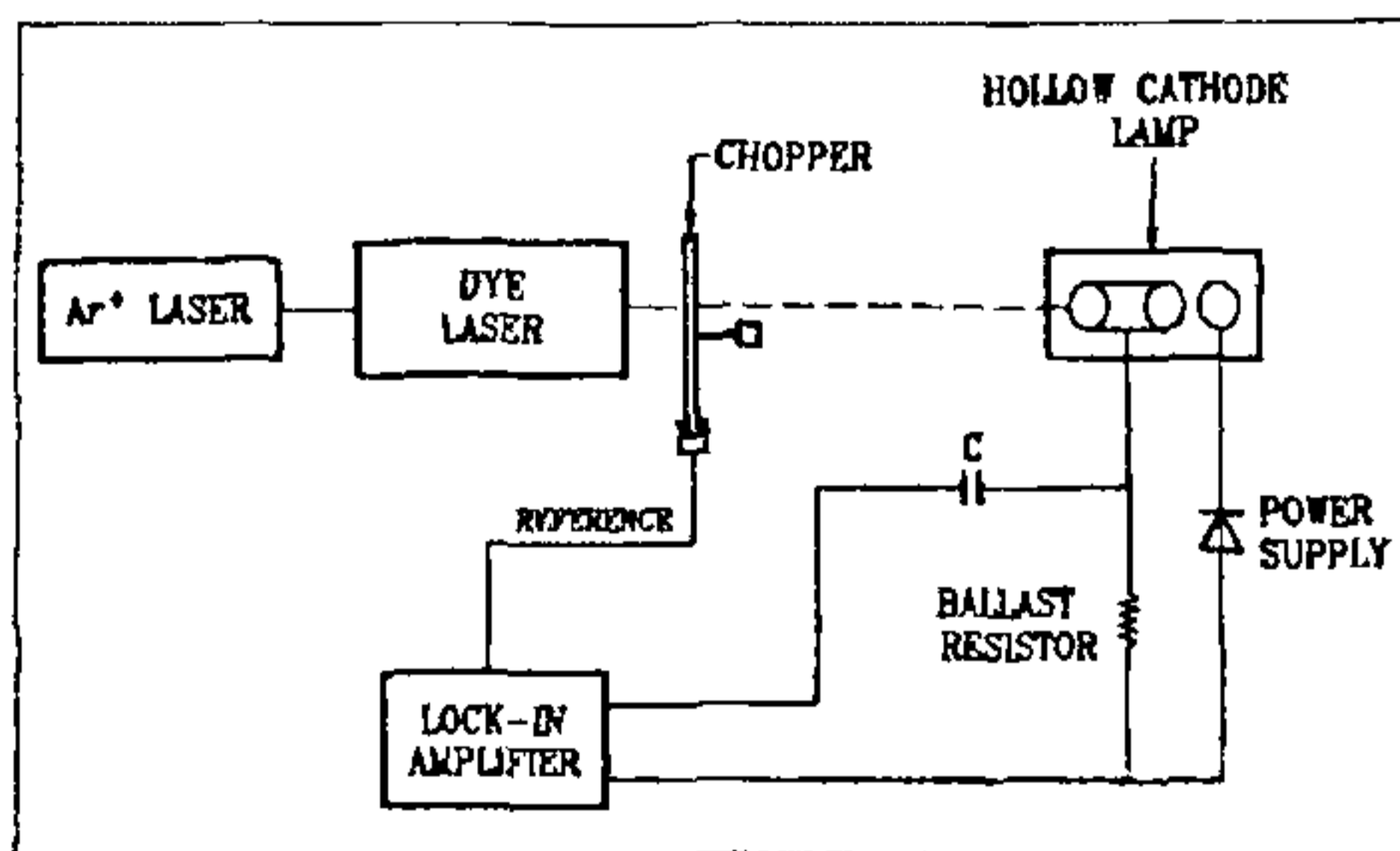


Figure 7. Experimental system for laser optogalvanic (LOG) spectroscopy with a hollow cathode lamp and cw dye laser.

information on population distribution, energy-transfer processes, etc. Some of these applications are illustrated by our studies on discharges of CO₂ (ref. 22), and NH₃ (ref. 23).

The ν₂ absorption region of NH₃ overlaps with CO₂ laser emission lines, and this has led to the development of the optically pumped NH₃ laser. It is possible that a similar laser system can be developed in ammonia discharges also. It is necessary to study the dynamics of the discharges for this purpose and we have done this using LOG technique.

The experimental set-up for the LOG studies is

shown in Figure 9. Radiation from the line-tunable continuous-wave CO₂ laser was chopped at 700 Hz and sent through the discharge and the optogalvanic signal was synchronously detected with a lock-in amplifier. The 10-μm region contains absorption lines corresponding to transitions from ground to ν₂ and ν₂ to 2ν₂ states. If we compare the normal absorption signal with the optogalvanic signal it can be seen that in the discharge, the ν₂ level is much more populated. By using the relative intensities of the various optogalvanic signals we could establish the following: (i) that the negative glow and positive column have different vibra-

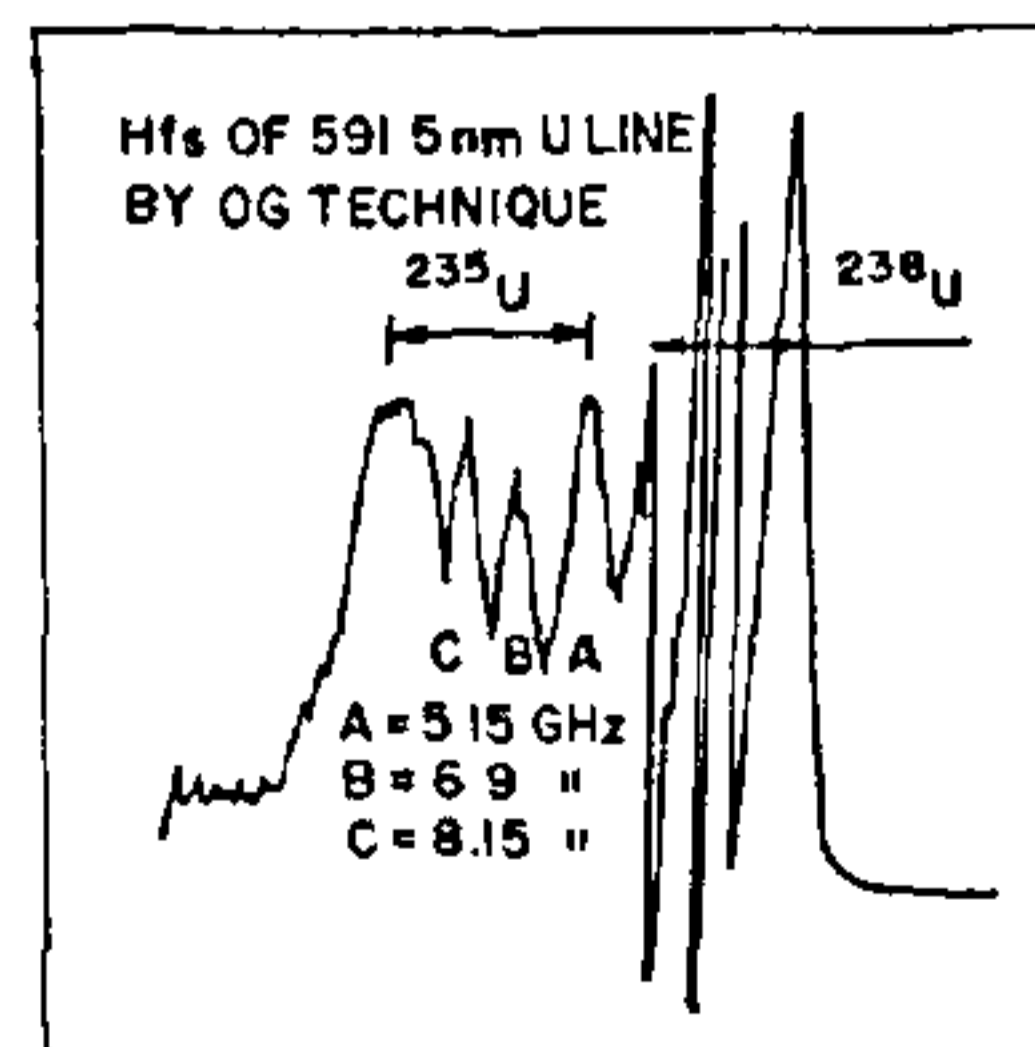


Figure 8. LOG spectrum of 591.5-nm line of uranium. The hyperfine structure (hfs) of ²³⁵U present at the natural concentration (0.7%) can be easily seen.

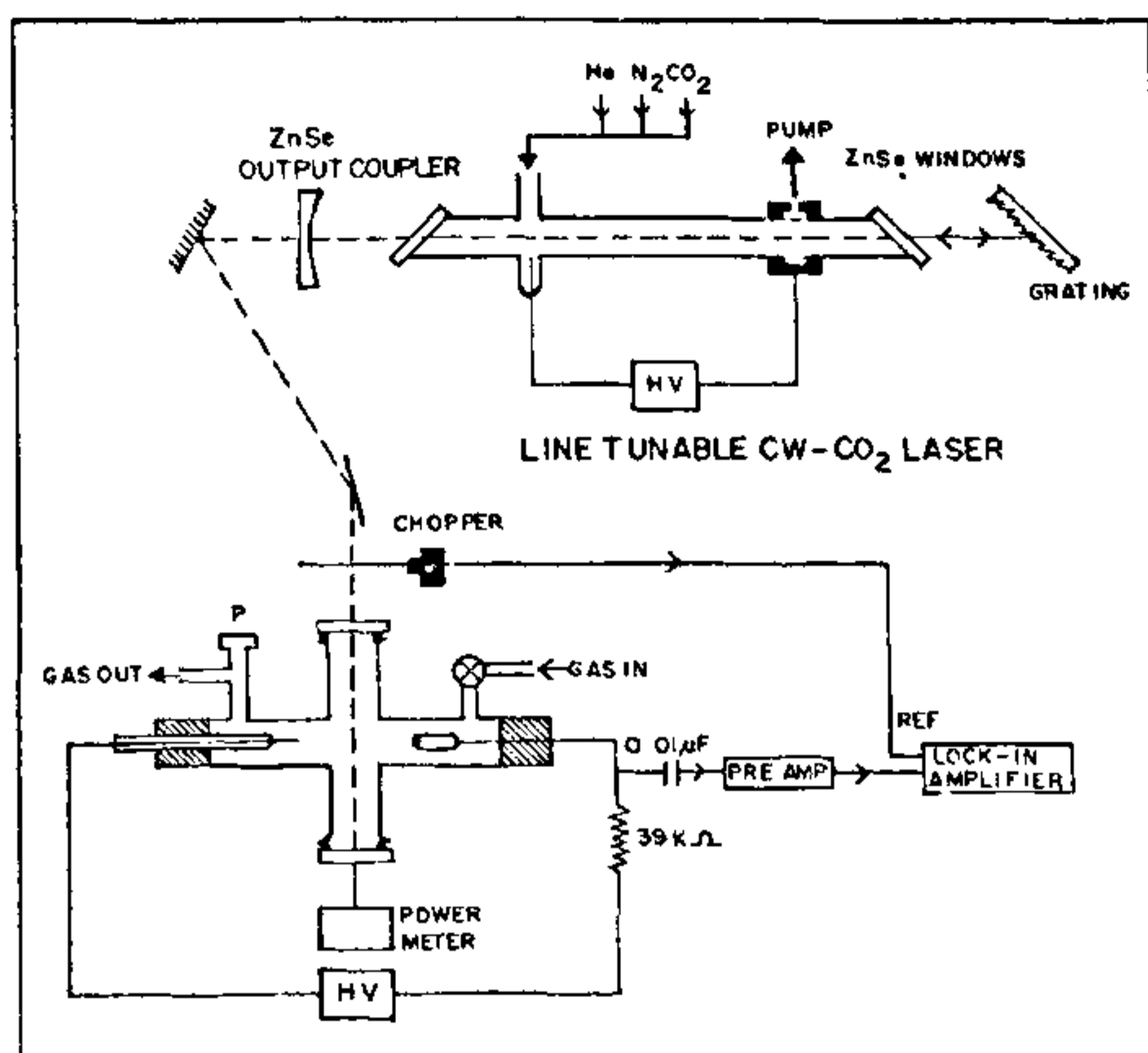


Figure 9. LOG set-up with CO₂ laser and d.c. discharge.

tional and rotational temperatures; (ii) that the population distribution in the two regions of the discharge follow Boltzmann distribution corresponding to the temperature of the region; and (iii) that there are levels that show anomalous behaviour, which could be explained in terms of the dynamics of energy-transfer processes.

All these are illustrated in Figure 10, which shows LOG

signal ratios for the same transitions observed in the negative glow and positive column as a function of the energy of the lower level of the transition for various CO₂ laser lines. The linearity of the plot proves (i) and (ii) above. The two transitions which lie considerably away from the plot show the importance of energy-transfer processes²³ in LOG signal production.

Another interesting aspect of spectroscopic studies on discharges is the time behaviour of such systems. An example is given by the results of our studies²⁴ on pulsed hollow-cathode discharges. In many experiments with atomic-vapour systems produced by various techniques in applications like laser fusion, laser isotope separation and laser deposition, it is necessary to know the nature of the various species, their interactions, lifetimes, etc. In our experiments to study some of these aspects, we have used a pulsed hollow cathode as the atomic-vapour source, and studied its characteristics by laser absorption spectroscopy. Figure 11 shows typical absorption characteristics of several transitions in a uranium hollow cathode as a function of time. The absorption at any time is directly proportional to the number density of the atoms in that level along the laser path. Detailed analysis of these absorption patterns gives information on processes like relaxation of atoms in the various levels, kinetics of ion-electron recombination, mechanism of post-discharge processes like Penning ionization, and diffusion of metal atoms in the vapour or diluent gas.

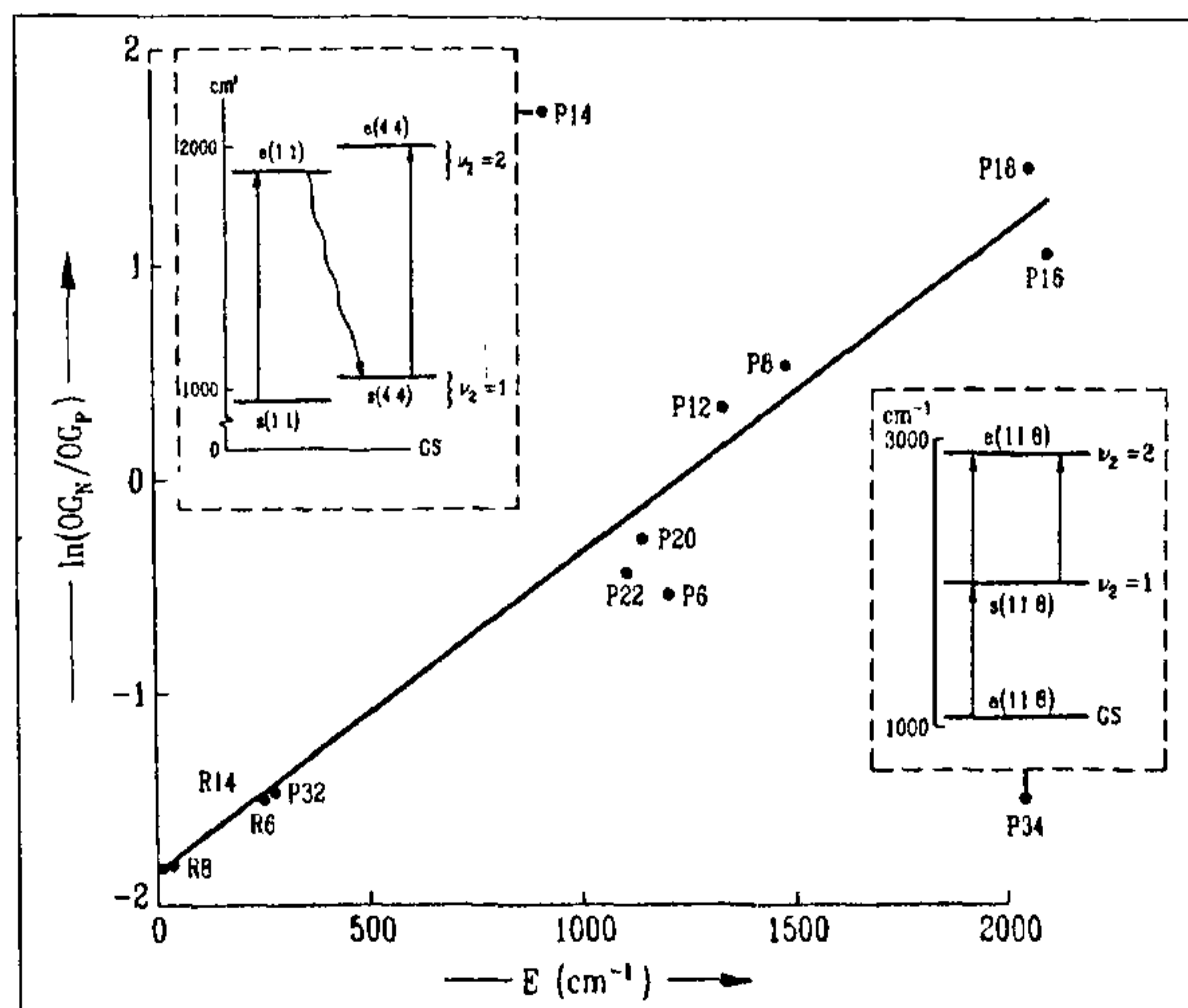


Figure 10. Ratio of OG signals in the negative-glow (OG_N) region to signals from the positive column (OG_P) in an NH₃ discharge. The linearity of the curve shows that both regions have a Boltzmann distribution, but with different temperatures. The insets correspond to transitions involving multiple steps and hence do not lie on the plot, namely P₃₄ and P₁₄.

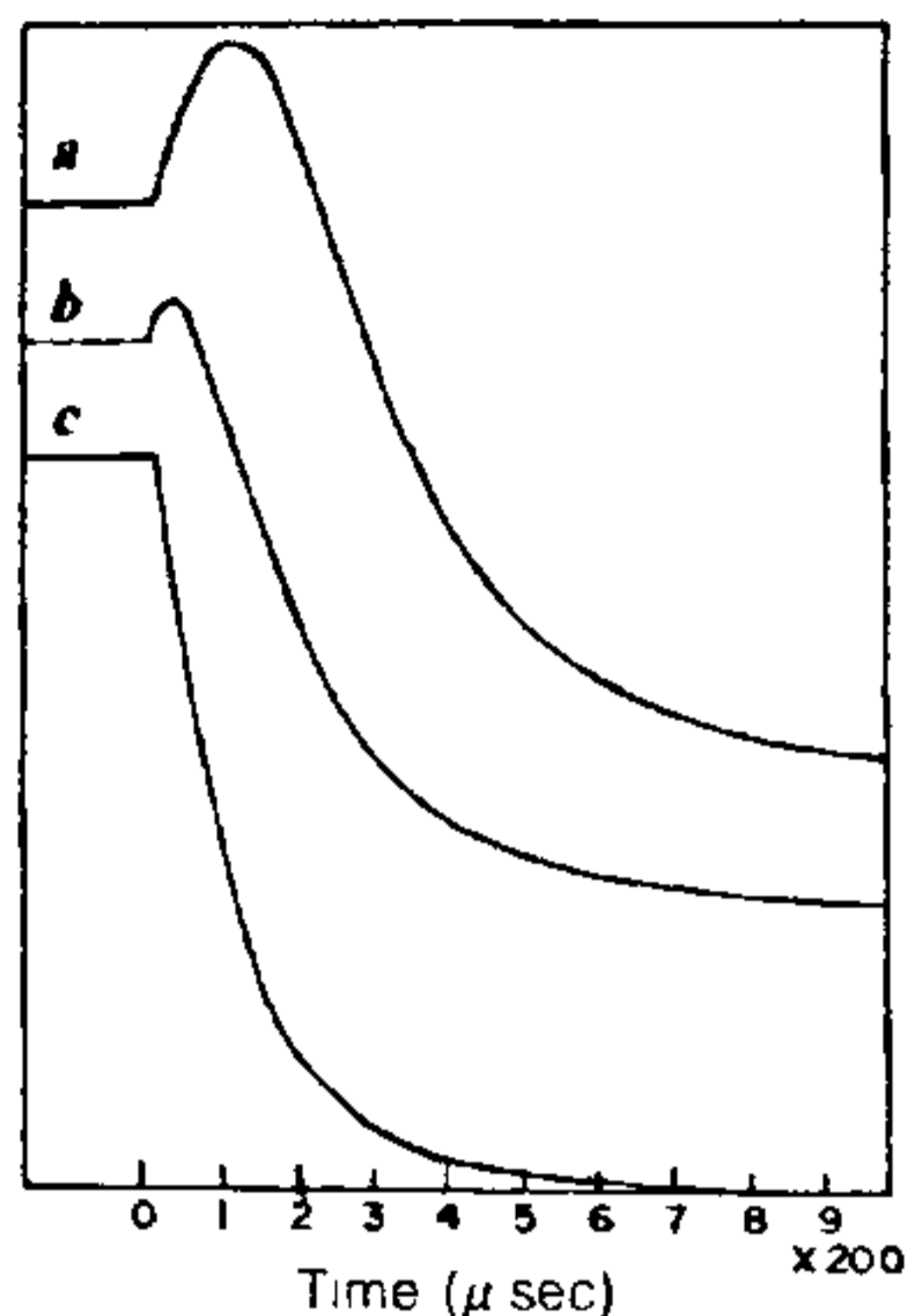


Figure 11. Population decay in uranium atomic levels in a pulsed hollow cathode, as seen by laser absorption. *a*, Lower state ground 5L_6 transition wavelength 591.5 nm; *b*, lower state 620 cm^{-1} 5K_5 , transition wavelength 597.1 nm; *c*, lower state 3800 cm^{-1} 5L_7 , transition wavelength 597.6 nm.

As an extension of this programme, we carried out studies in relaxation processes in laser-produced plasmas of metals. The plasmas were produced by focusing 200 mJ from an XeCl laser at 308.0 nm on a rotating target in a vacuum chamber. The emission from the plasma was recorded with a 0.5-m monochromator and cooled photomultiplier. Typical spectral patterns close to the target and away from the target are shown in Figure 12 for a copper target. Identification of the transition showed that several levels above the ionization limit are highly populated²⁵.

Supersonic beams and clusters

There is considerable interest at present in new types of molecules that are normally unstable but can be produced under special conditions. Atomic and molecular clusters, van der Waals' molecules, and transient species produced under various experimental conditions are of great interest in several areas like catalysis, structure and interaction of molecular species, and reaction kinetics. Laser spectroscopy provides one of the best techniques for obtaining detailed information of such species.

In the case of systems like metals, laser ablation provides one of the convenient techniques for production of clusters. In the experiment on copper mentioned earlier, the Cu atoms produced can undergo collisions either among themselves or in presence of other gases, leading to cluster formation, which could then be detected by suitable laser-spectroscopy techniques like fluorescence. This is shown in Figure 13, where copper dimers produced during XeCl laser evaporation are

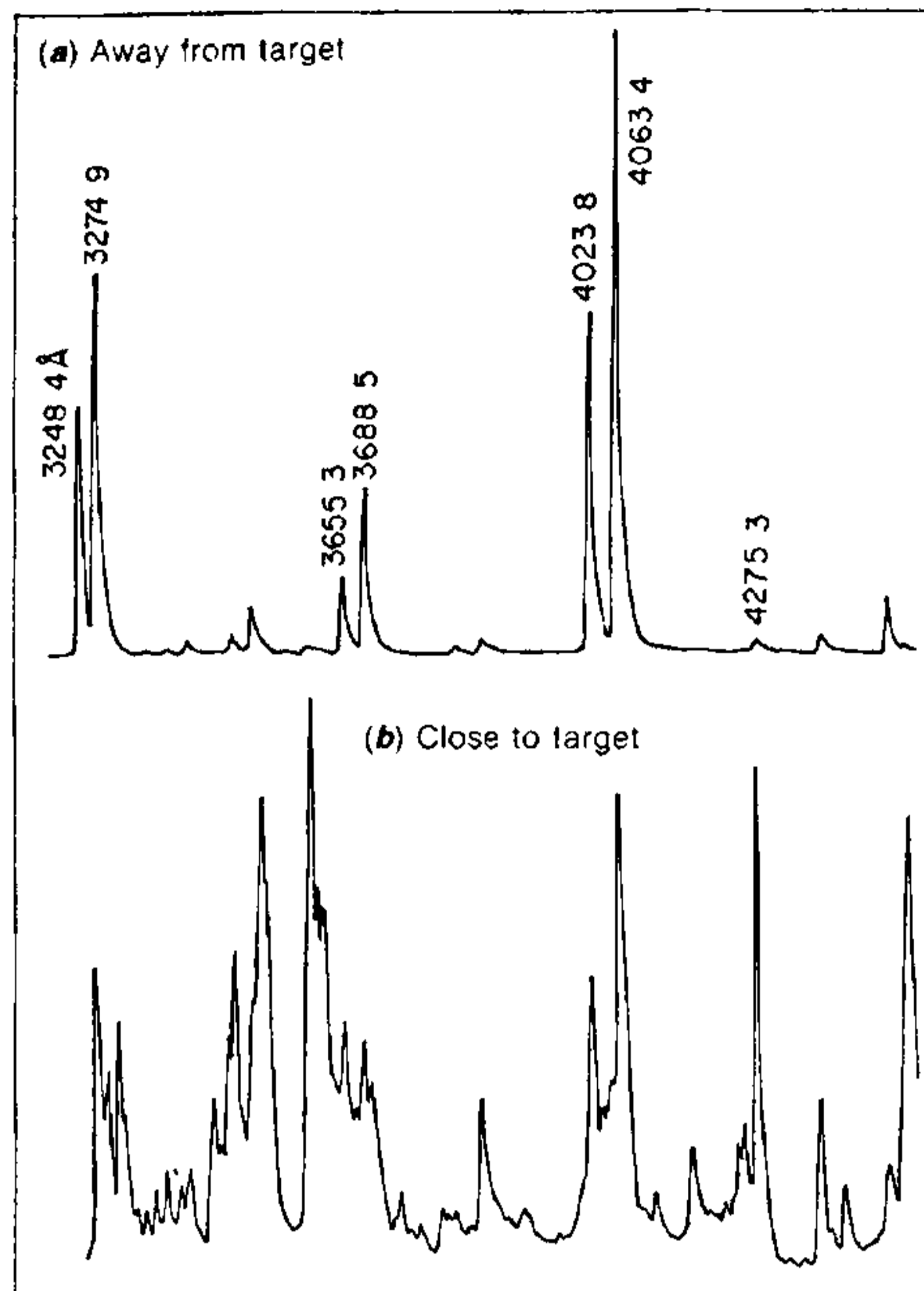


Figure 12. Spectra of excimer laser (200 mJ)-produced plasma of a copper target. Close to the target (*b*) we see many more lines, arising from the $3d^9 4s ns, np, nd$ autoionizing levels. These decay to the $3d^{10}$ series, which persist for larger distances (*a*)

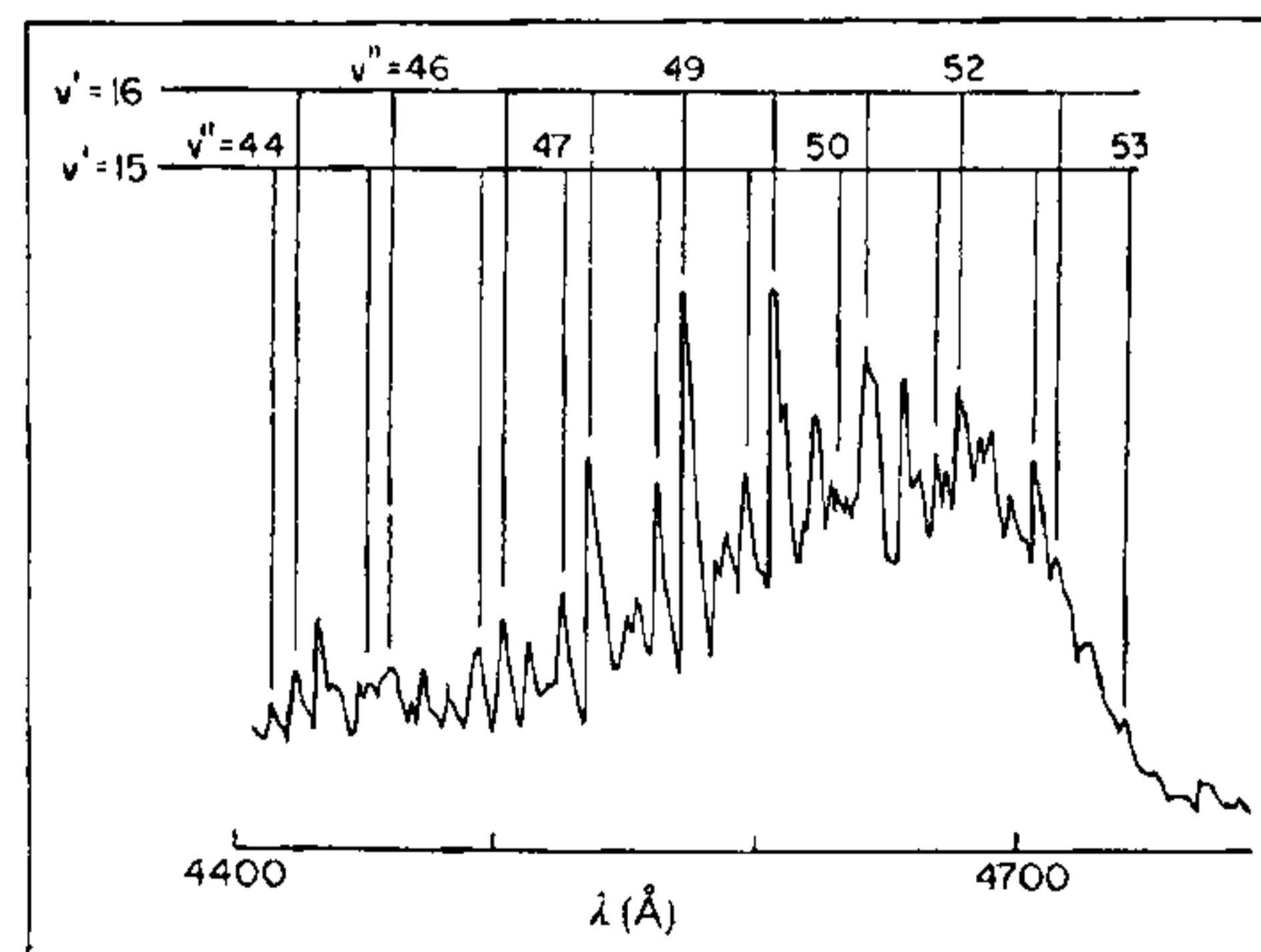


Figure 13. XeCl laser-induced fluorescence from Cu_2 dimers formed in an excimer laser-produced copper plasma.

detected, on excitation at the same wavelength, by fluorescence from the excited dimers²⁶.

Clusters, van der Waals' molecules, and many other

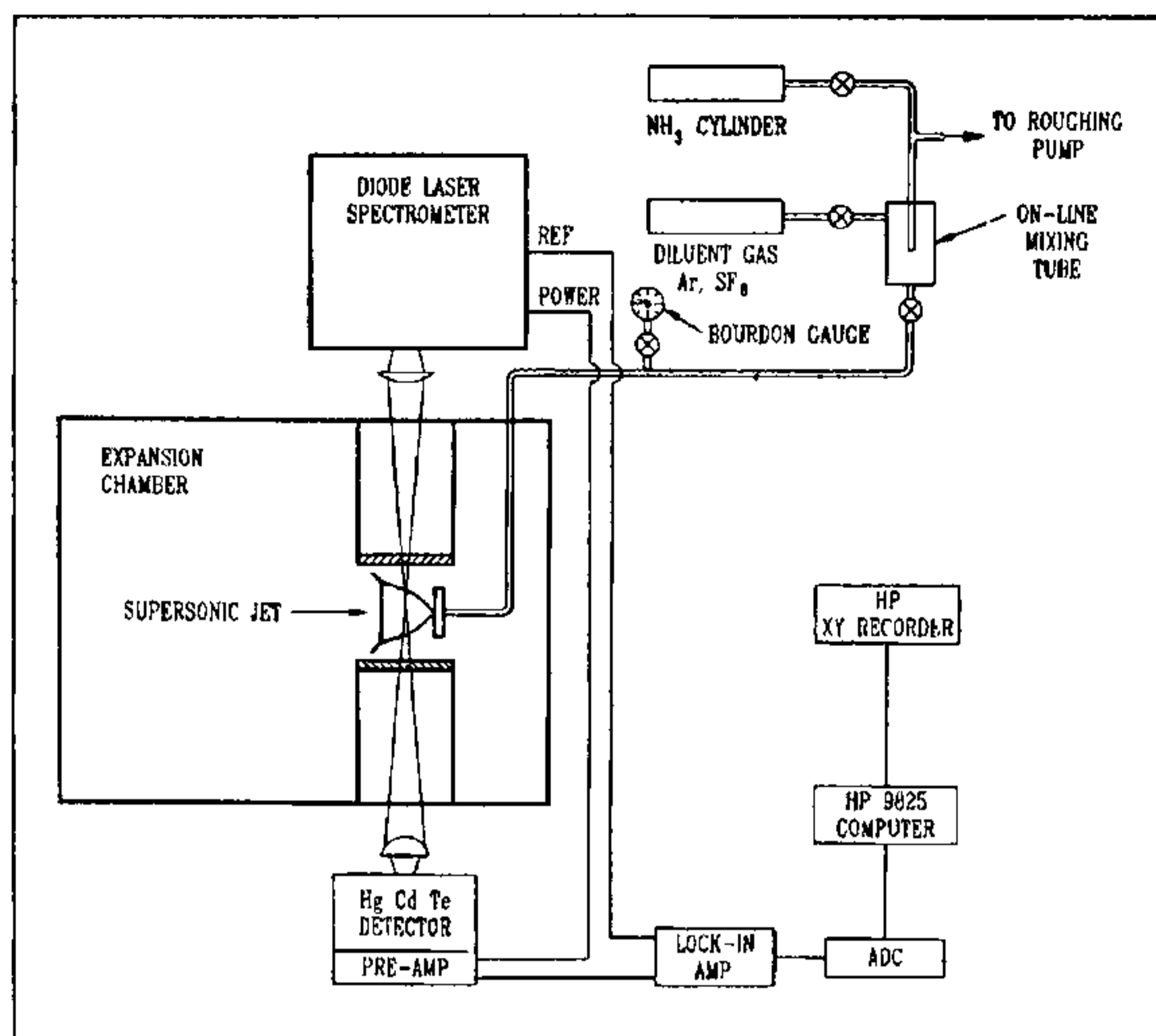


Figure 14. Experimental set-up for diode laser absorption studies in supersonic molecular beams.

transient species can be conveniently produced and maintained for sufficiently long periods in supersonic nozzle beams. In a supersonic nozzle beam, the species of interest (pure gas, discharge products, high-temperature species, etc.) are mixed with an inert carrier gas like helium. The mixture, under high pressure, is allowed to expand through a nozzle into a vacuum chamber. Under conditions of isentropic expansion, the system cools down to very low temperatures without change of phase, attaining translational temperatures of the order of 1 K, with rotational temperatures closely following. The supercooled beam thus provides an ideal environment for any unstable species, with the added advantage that the low temperatures provide a much simpler spectrum.

In the Spectroscopy Division in BARC, we have set up²⁷ a supersonic nozzle beam system for spectroscopic studies using diode laser techniques. A schematic diagram of the experimental set-up is shown in Figure 14. Spectra of SF₆ obtained under various conditions in this set-up are shown in Figure 15. Detailed information has been obtained on dynamics of such beams²⁸⁻³⁰. An interesting spectroscopic evidence for condensation

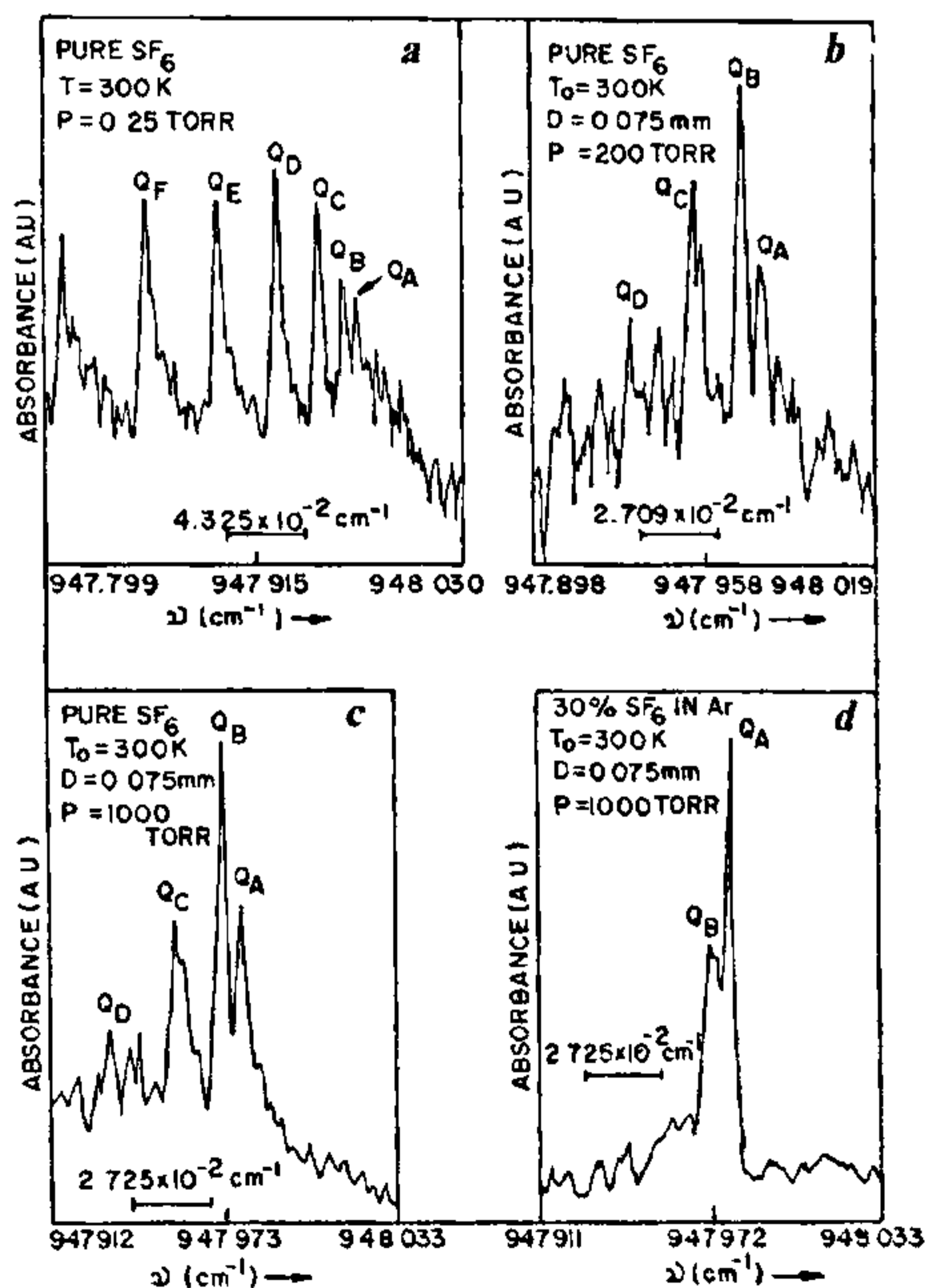


Figure 15.

Figure 15. Diode laser absorption spectrum of nozzle-cooled SF₆. Q_A, Q_B, etc. correspond to Q branch band heads formed at progressively higher rotational quantum numbers. *a*, room-temperature static cell, *b* and *c*, supersonic beam, pure SF₆; *d*, supersonic beam with argon diluent. The disappearance of higher band heads show the rotational cooling

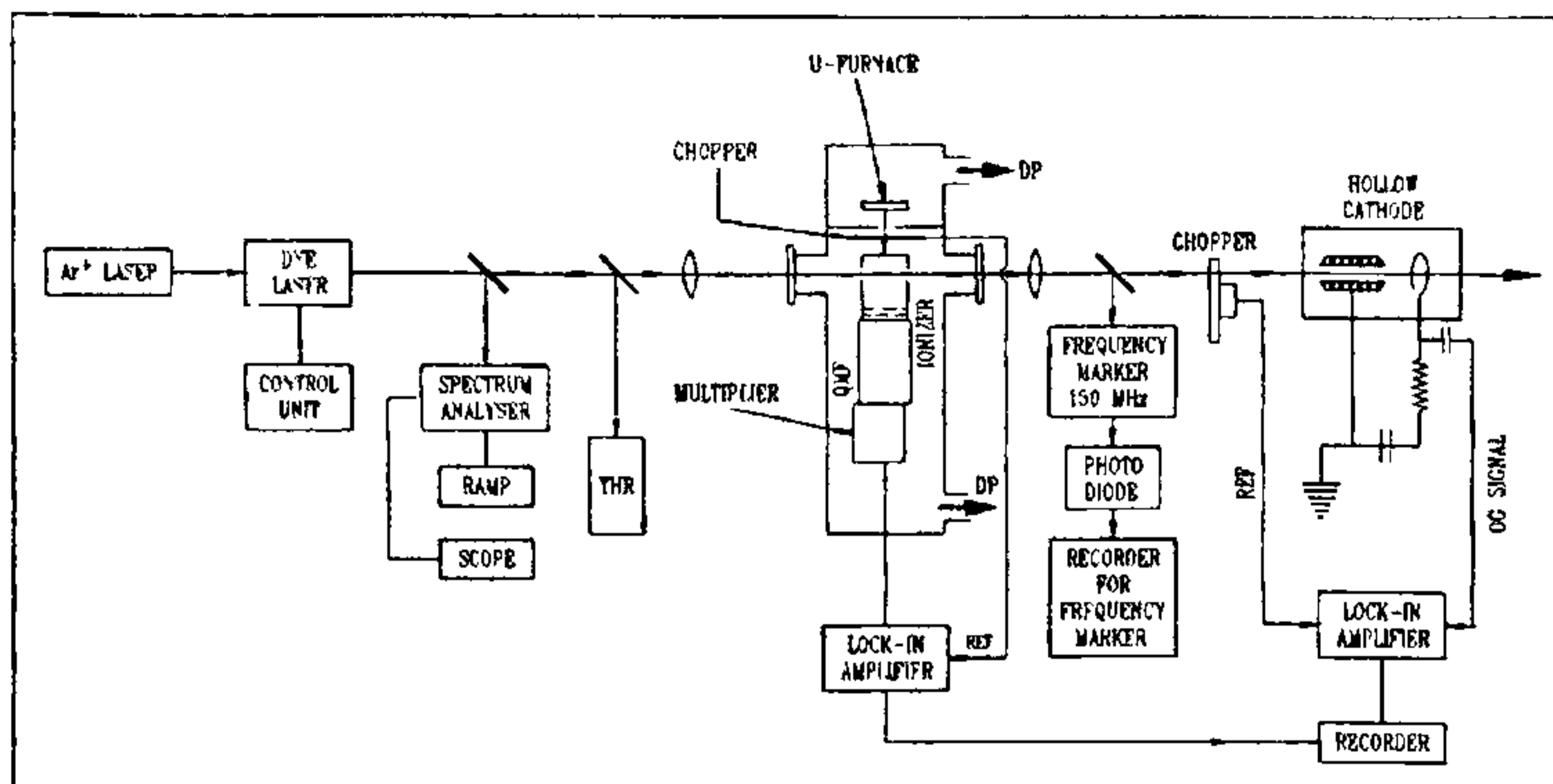


Figure 16. Experimental set-up for study of laser-enhanced chemi-ionization of uranium.

in such beams is provided by the so-called splitting of single lines, arising from depletion of absorbing species in the central portion of the beam³⁰. More details of spectroscopic studies on such beams are given by other authors³¹⁻³³.

Chemical dynamics and laser spectroscopy

The applications of laser spectroscopy to problems in chemical dynamics are too numerous to be listed here completely (see for example refs. 34-36). As a simple example I briefly discuss here some of our results on laser-enhanced chemi-ionization of uranium³⁷ with oxygen. In collisions between thermal uranium atoms and molecular oxygen, two reactions take place. One is the oxide formation



and the second, the associative ionization



Under normal conditions, reaction 1 has a cross-section equal to 99% of the total reaction cross-section, while only 1% of the total cross-section arises from reaction 2. If the U atom can be excited to a higher electronic state, these cross-sections may change drastically, since, in laser-assisted collisional processes, any collisional interaction allowed in first order will have a laser-induced analogue in higher order, which could increase the cross-section to a value greater than the gas-kinetic cross-section and also open up channels blocked in first order by selection rules or energy-conservation requirements³⁸.

Our experimental set-up is shown in Figure 16 and a typical scan in Figure 17. The increased signal on laser excitation can be used for quantitatively estimating the

cross-section for reaction 2. This gives an enhancement for reaction 2 by a factor of 1000, due to laser excitation.

Though a detailed interpretation of the enhancement is very difficult, a qualitative understanding of the effect can be obtained from approximate potential-energy curves showing the various possibilities of U-O₂ interaction. This is given in Figure 18, which shows that the enhanced cross-section can arise from long-range potential-energy curve crossing for (U*+O₂) and (UO₂⁺) compared to (U+O₂) with (UO+O) (ref. 37). Further understanding of the dynamics will require more detailed studies involving excitation to various levels, and also the use of other reactants than oxygen.

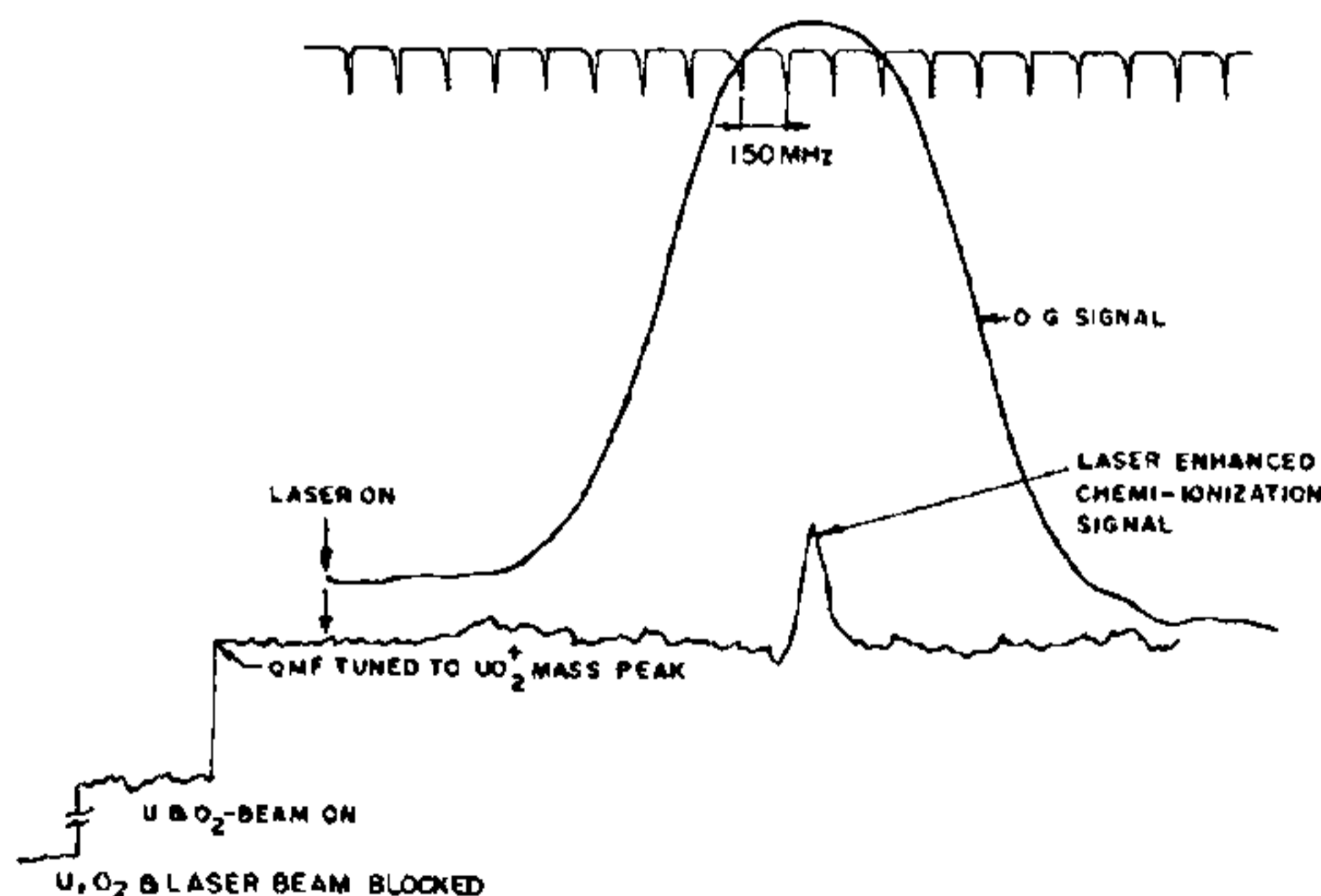


Figure 17. Laser-enhanced chemi-ionization of uranium with oxygen. The laser-enhanced chemi-ionization signal arises from a volume of 0.0002 cm³, where the laser, U atomic beam, and O₂ molecular beam overlap. The number density of U atoms in this region is 3 × 10⁶ cm⁻³.

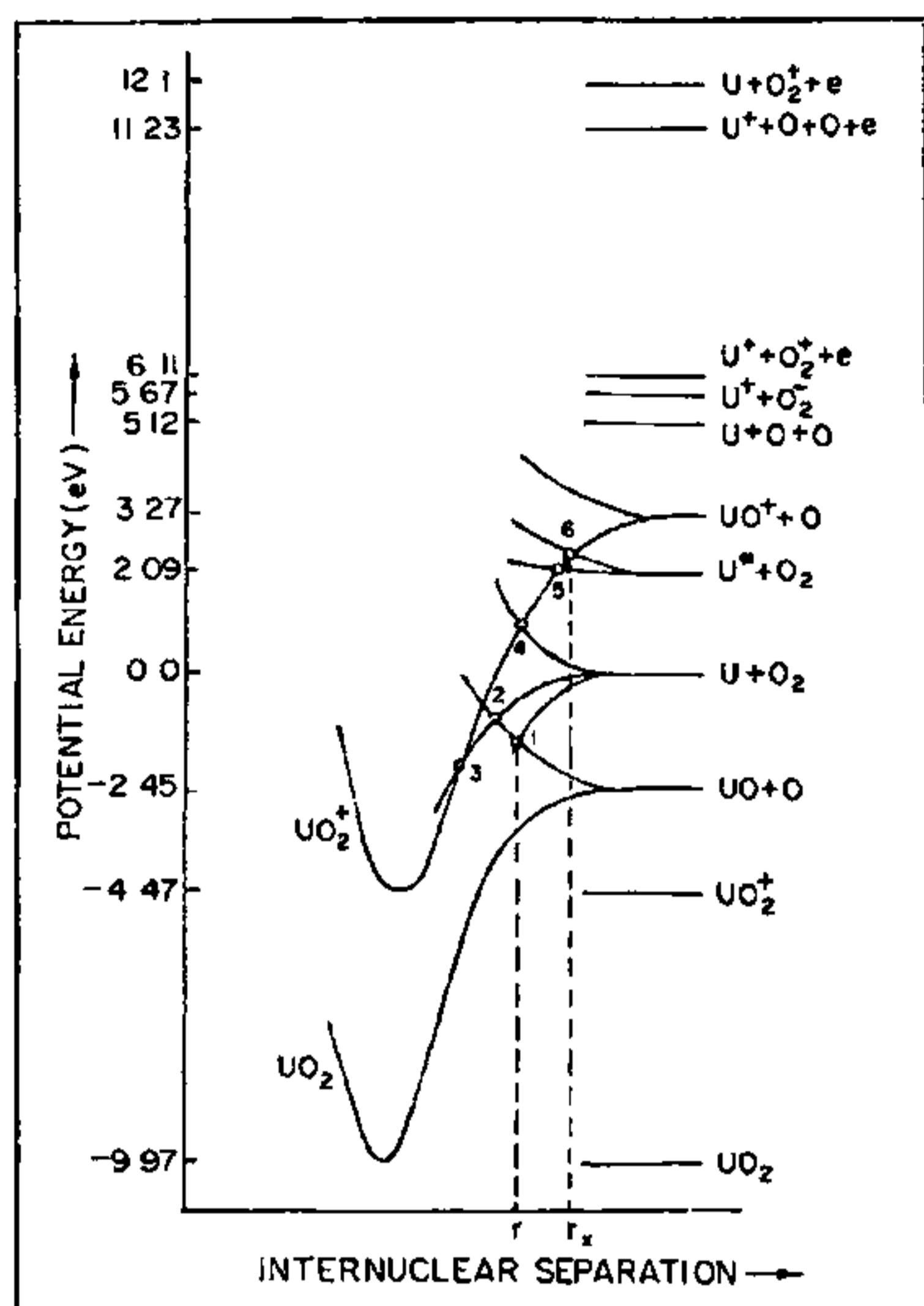


Figure 18. Energy levels of $U+O_2$ system. The potential energy curves are only schematic. The energy values at minima and infinity are taken from the literature

Summary

Laser-spectroscopy techniques can be applied very efficiently in many fields to gain complete and correct understanding of the problems in that field. Thus studies in areas as diverse as ultra-trace analysis, high-energy physics, chemical dynamics and catalysis can be successfully pursued by making use of laser-spectroscopy techniques, which provide information on initial-, intermediate- and final-state parameters in any process.

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