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DEVELOPMENT OF LASER-BASED TECHNIQUES FOR
IDENTIFICATION OF BREACHED NUCLEAR FUEL
ELEMENTS IN STORAGE

MASTER

Richard J. Anderson, Peter Esherick

Prepared by Sandia Laboratories, Albuquerque, New Mexico 87115
and Livermore, California 94550 for the United States Atomic Energy
Commission under Contract AT (29-1)-789

Printed June 1980

Sandia National Laboratories

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SF 1004-DF(11-77)

Printed in the United States of America
Available from
National Technical Information Service
U. S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161
Price: Printed Copy \$3.50; Microfiche \$3.00

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Printed May 1980

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OF BREACHED NUCLEAR FUEL ELEMENTS IN STORAGE *

PROGRESS REPORT 1978 OCTOBER 1 TO 1979 SEPTEMBER 1

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ABSTRACT

From many possible laser-based techniques of atomic and molecular spectroscopy we have selected multiphoton ionization spectroscopy (MIS) as that one technique which best conforms to the constraints imposed by the problem of identifying breached nuclear fuel assemblies in storage. We describe experiments utilizing MIS to specifically and sensitively detect xenon (Xe) and nitric oxide (NO). We therefore experimentally demonstrate the applicability of this technique to the detection of volatile fission products leaking from breached nuclear fuel assemblies stored in water cooled basins. Even for the non-ideal circumstances of these preliminary experiments we estimate a detection limit of 10^{10} atoms/cm³ for xenon, roughly one percent of the atmospheric content of xenon at sea level.

*This report was prepared for the Department of Energy, Away from Reactor Spent Fuel Storage, under contract # DE-AC04-76DP00789.

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DEVELOPMENT OF LASER-BASED TECHNIQUES FOR IDENTIFICATION OF BREACHED NUCLEAR FUEL ELEMENTS IN STORAGE

Summary

The long-term storage of spent nuclear-fuel assemblies in water-cooled basins requires a sensitive monitoring capability to assure that environmental standards are met for the release of radioactive fission products. The presence of fuel assemblies with pinhole leaks (leakers) must be determined, and these assemblies must be located and subsequently isolated to prevent possible breaches in the fuel rods which could release significant quantities of volatile fission products (e.g., ^3H , $^{14}\text{CO}_2$, Kr, Xe). The purpose of this study has been to evaluate laser-based monitoring technology as a means of locating these "leakers".

We have examined potential laser-based measurement techniques for this particular application. A viable technique must sensitively, selectively, and quantitatively measure the concentration of the species of interest. From all possible candidates considered, we have selected, for more intensive study in the laboratory, the detection of multiple-photon absorption by photoionization of the excited species: multiphoton ionization spectroscopy or MIS. Based on our laboratory research, we estimate a detection limit for xenon of $10^{10}/\text{cc}$ using a one-millijoule/pulse laser. Because of the large intensity dependence of the MIS process, we predict a vast potential improvement in sensitivity by increasing the laser intensity. This has not yet been fully observed due to complications arising from intensity dependent broadening and energy shift of the resonant level. However, even with these complications, the overall result shows high sensitivity and considerable wavelength selectivity.

In the course of our laboratory studies, we demonstrated on nitric oxide (NO) that the high selectivity shown in molecular infrared absorption can be combined with the high sensitivity of MIS. We selectively ionized molecules originating from a single rotational state by tuning an infrared laser to the appropriate rotational-vibrational transition and by tuning a visible laser to the appropriate two photon transition. At 1 Torr NO pressure there is no detectable direct IR absorption, but the IR plus visible, multiple resonance MIS spectrum shows at least 20:1 signal over background.

We propose now to pursue the MIS study of xenon using a lower-order multiphoton process to do the ionization. An increase in the sensitivity of detection will result while the effects of intensity dependent broadening and level shifts will be reduced. We will ascertain the necessary information for a full evaluation of this technique as a practical monitor for leakers. We also propose to continue the studies on the IR plus visible MIS. These studies can be extended to $^{14}\text{CO}_2$ to develop a measurement technique for this molecule that promises to set new limits of selectivity and sensitivity.

Introduction

In underwater storage facilities, the spent nuclear fuel is usually stored in the original fuel assembly containers. Since this spent fuel has not been processed, the actinides, fission products, and other radioactive material are still present. As long as the fuel rods are not breached, these radioactive materials are contained. If breached, the volatile fission products can leak out. Since a fraction of the received fuel assemblies are known to leak on receipt and others can develop leaks in storage, it is important to determine which fuel assemblies are leaking so that they can be isolated. The purpose of this study has been to evaluate laser-based monitoring technology as a means of locating these "leakers".

We have analyzed several possible laser detection techniques in the light of various constraints. A viable technique must sensitively, selectively, and quantitatively measure the concentration of the species of interest, whether they are atoms or molecules. The potentially interfering processes must be minimal. For example, interfering absorption of the laser by a background gas cannot be tolerated, and absorption of fluorescence by another species is unacceptable. Because we are concerned with rare gases and other species with relatively high-lying electronic levels, the measurement technique must be capable of effectively operating in the energy regime equivalent to the vacuum ultraviolet.

All laser-based measurement techniques that rely on single photon absorption are poor candidates for use since no tunable laser exists in the vacuum ultraviolet region. Since atoms have only electronic degrees of freedom, techniques which detect only changes in molecular vibrational

state have also been discarded. Thus direct infrared absorption, spontaneous Raman scattering, and all various nonlinear Raman techniques (CARS, RIKES, and stimulated Raman gain or loss) are unsatisfactory. The most likely techniques are those based on resonant nonlinear (i.e., multiphoton) absorption of tunable laser light in the visible and near ultraviolet. This requires the use of pulsed lasers and the detection of a very small number of excitations which could be as few as one per pulse. Thus, optoacoustic detection of the time integrated signal is not practical. Optogalvanic detection of rare gases in a discharge is a promising technique for our applications. However, in the optogalvanic detection process, there is an inherent background level that determines minimum sensitivity. In addition, the discharge can change the chemical composition of the species and greatly interfere with the quantitative capability of the technique. Since we were searching for a general technique and one of great sensitivity, we do not advise the study of the optogalvanic method at this time. Fluorescence-detected multiphoton absorption is a strong candidate for laboratory study, but it suffers from two main problems: first, reabsorption of the emitted light and, second, collisional quenching can affect the quantitative nature of the measurement.

We have chosen for further study the most promising technique for the detection of xenon and krypton and probably the most promising one for tritium (^3H) and carbon-14 substituted carbon dioxide ($^{14}\text{CO}_2$) -- multiphoton ionization spectroscopy, MIS. We have identified MIS as the most promising laser-based technique for four reasons. First, it is a fundamentally simple experimental technique. A tunable laser of appropriate intensity and wavelength is focused into a sample

cell. The atoms in the laser's focus are ionized by the multiple absorption of laser photons. The resultant free ions and electrons are collected by a pair of electrodes to produce an easily observable electrical signal that is proportional to the number of atoms ionized by the laser. The second reason that this technique is attractive is that the efficiency of detecting ions can be very high. In fact, with particle detection techniques developed by the experimental nuclear sciences, it is possible to detect a single ionization event and thereby the presence of a single atom in the laser's focus.¹ The third advantage of the technique is provided by the tunability of the laser, which allows one to precisely select a wavelength that optimizes the ionization of the atoms of interest while minimizing the undesirable signal due to background species concentrations. And finally, the technique is general, applicable not only to atoms, but also to molecular species.^{2,3} This will be discussed in "Double Resonance MIS of Molecular Species," below.

The development of a successful MIS monitoring technique requires that adequate research be done to make full use of the advantages that the technique offers. The most critical parameter to be determined for a given process is the saturation intensity, which is the intensity above which all atoms of interest in the focal volume are ionized. Since at sufficiently high laser intensity every species present will ionize, it is also necessary to find, for each atom of interest, an optimum wavelength where the saturation intensity is a minimum. Use of this optimum wavelength has distinct benefits: not only does it reduce the intensity requirements for the laser used, but it can also greatly improve the selectivity of the process and its immunity to interference by background signals.

For any given atom there will be a large number of wavelengths where the multiphoton ionization signal is resonantly enhanced. This enhancement occurs whenever the energy of one laser photon or the combined energy of a number of laser photons equals the energy of an electronic level in the atom. One-photon resonance is shown in Fig. 1a. In this excitation scheme, for cesium (Cs), resonance is achieved by tuning the laser to the excitation energy between the 6s ground state and the 7p excited state. Once excited to the 7p state, the Cs atom is readily ionized by absorption of a second photon, into the ionization continuum.¹ Two-photon resonance enhancement is also possible (Fig. 1b), as illustrated for strontium (Sr). Here, it is the energy of two photons that just equals the excitation energy from the ground state to some 5snd 1D_2 state. By scanning the laser wavelength, a multitude of resonances in the ionization signal are observed⁴ corresponding to resonances with each of the 5snd 1D_2 Rydberg states.

By using more than one laser, it is possible to simultaneously achieve more than one resonance, as shown for barium (Ba) in Figure 1c. In this case the wavelengths of three lasers were chosen such that the first laser excited Ba atoms from the 1S_0 ground state to the low lying $^3P_1^0$ state. Photons from the second laser then caused excitation from this $^3P_1^0$ state to a higher lying $3S_1$ state. The wavelength of the third laser was then scanned, allowing the observation of resonances involving still higher energy $^3P^0$ and $^1P_1^0$ Rydberg states. Even with this fairly complicated excitation scheme, strong resonances were very clearly observed in the ionization signal which resulted from the laser excitation. In fact, by using these multiple resonances, strong signals were still very easily observed⁵ even when two of the laser beams were attenuated by factors of up to 1000. It is

precisely this phenomenon that one hopes to exploit in making MIS a very selective detector of the particular atoms of interest. By the proper choice of wavelength, laser intensity requirements can be very modest, and the resonant enhancement in the desired atom can provide signals many orders of magnitude above background.

Each different excitation scheme, with its different possible intermediate state resonances, constitutes an excitation pathway. A pathway is often selected primarily on the basis of the available wavelengths of laser radiation. However, alternate, multiple-resonance pathways are often selected to achieve desired goals, e.g. spectroscopic study of otherwise inaccessible excited states and increased selectivity in detecting desired species.

We now turn our attention to the atoms of interest, such as Xe, and investigate what type of excitation pathways are accessible for these atoms. The most obvious difference between these two atoms and those discussed above is that they have considerably higher ionization potentials. This means that pathways using visible photons will require at least five photons to ionize these atoms. Similarly, because these atoms do not have any low lying excited states, the majority of the resonance enhancements to be observed with visible photons will be from 4-photon resonances. In spite of these apparent drawbacks, we have opted to initiate our studies with the investigation of the five photon ionization of Xe with four photon resonance. Our reasons for this choice are as follow:

- 1) High intensity (200 kW) laser pulses at the wavelengths required for these experiments were obtainable with existing tunable sources
- 2) The family of accessible 4-photon resonances includes a significant number of different excitation pathways. We have been

able to study resonances to several of the $(5p^5)np$ and $(5p^5)nf$ states, from which we have been able to elucidate some important trends useful for classifying promising excitation pathways.

- 3) The 4-photon resonant, 5-photon ionization pathways constitute, in many respects, a worst case that requires much higher laser intensity than the lower-order (2- or 3-photon resonant) processes more commonly studied. At high intensities, any number of intensity dependent optical phenomena may occur as side effects to the multiphoton ionization. (For example, intensity dependent wavelength positions and widths of resonances.) Because these side effects are more dominant for a high- rather than a low-order process, a high-order process can provide a better test case for evaluating their importance.

The difficulties described here for atoms of high ionization potential are exacerbated for small molecules by the rotational and vibrational degrees of freedom. These spread out the electronic spectrum, resulting in overlapping lines of lower spectral strength which adversely affects selectivity and sensitivity. We report the results of preliminary experiments on nitric oxide (NO) in which we use these degrees of freedom to our advantage by exciting first in the sharp, sparse pure rotation-vibration spectrum (first photon of Fig. 1c), then exciting and ionizing with a visible laser for highly sensitive detection of the infrared spectrum of a specific molecule.

Apparatus

Figure 2 shows a block diagram of the experimental apparatus. The pump laser is the third harmonic of a Nd^{+3} :YAG laser at 354.7 nm; typical pump energy is 22 mJ per pulse at ten pulses per second. We have constructed our own dye laser oscillator after the design of Littman⁶ using a grazing incidence grating (2400 lines/mm, 50 mm diameter) and a Littrow grating (800 lines/mm, blaze = 800.0 nm, used in second order). This laser is continuously tunable from 462.3 nm to 418.1 nm with a full width at half maximum bandwidth of 0.004 nm (0.2 cm^{-1}). Two amplifier stages increase the dye laser output to 0.5 to 1.5 mJ per pulse, depending on the dye gain curve. Maximum intensity is thus about 200 kW to 600 kW in a pulse whose full width at half maximum is 4 nsec. We usually use a 100 mm focal length lens which reduces the beam waist at focus to about 0.040 mm diameter in the cell, giving a maximum flux of order 10^{10} W/cm^2 .

The ionization cell has two circular parallel plate electrodes (2 cm in diameter separated by 1 cm) that are mounted in a controlled atmosphere housing. The charge collected on the positively biased plate (i.e., the electrons) is integrated with a charge-to-voltage preamplifier with a sensitivity 0.5 V per picocoulomb and is averaged with a gated integrator (boxcar detector). The ionization signal, laser energy, and laser bandwidth monitor are recorded on a strip chart recorder and also read by a microprocessor which stores the data on a "floppy" disk.

We can control the mode structure of the pump laser to be either single mode (smooth time evolution) or multimode (highly structured time evolution), and in addition we can accumulate data only from single mode or multimode pumping. The dye laser time evolution largely follows that of the pump. Discrimination between the two types of laser pulse has been critical in

understanding the intensity dependent effects that occur in this five photon ionization.

Results and Discussion

Table 1 lists the observed states, together with the four photon wavelength and the relative maximum ionization signal of each. The states are labeled by angular momentum quantum numbers as well as the orbital to which the excited electron is raised (see Moore¹). We have observed only states of even total angular momentum (integers) for this even photon resonance. Also, for both the nf and np Rydberg series the greatest ionization strength lies in the lowest members.

We have also estimated the sensitivity of the experiment by measuring the number of ions made only by multiphoton ionization at the wavelength for maximum signal. The imposed bias was 5 V, so no secondary ionization could occur, and only the primary charge was collected in the limit of no losses due to ion recombination. For 1 mJ/pulse approximately 0.2 picocoulomb was collected, which corresponds to 10^6 electrons. The 0.3 torr pressure gave 10^{10} atoms per focal volume (about 10^{-6} cm³) so the ionization fraction is 1 in 10^4 . With suitable amplification by secondary ionization in a background gas [proportional counter operation] we can easily see an average of one ionization event per pulse, or a density of 10^4 atoms per focal volume. Therefore a conservative estimate of greatest lower bound for xenon detection is a partial pressure of 10^{10} per cm³, or 0.3×10^{-6} torr.

One might expect that increasing the power per pulse with constant focusing optics would give a higher ionization fraction. For example, commercial dye lasers are available which produce 10 mJ average energy

in a 4 nsec pulse. A tenfold increase in instantaneous intensity for a five-photon ionization should increase the ionization efficiency by 10^5 , which implies that every atom in the focal volume described above would be ionized. We have found for the five-photon ionization of xenon that this is complicated by the occurrence of intensity dependent effects in addition to ionization: changes in state energy and linewidth.

We can quickly describe a theoretical basis for these effects. The simplest phenomenological expression for the instantaneous five-photon ionization rate, as a function of intensity (I) and detuning from resonance ($\Delta\omega$) is

$$\text{Rate} \propto \frac{I^5 \Gamma}{(\Delta\omega)^2 + \Gamma^2/4}$$

This assumes that the energy of the resonant level is independent of intensity and that the linewidth (Γ) is due to relaxation from the resonant level via randomly occurring events such as fluorescence or collisions. However, at intensities necessary for five photon ionization, the resonant level is coupled to all other discrete and continuum atomic states by a non-resonant scattering interaction which shifts the state energy. This effect, called the dynamic (or AC) Stark effect⁸ causes the detuning to be intensity dependent; that is $\Delta\omega$ becomes $\Delta\omega + \delta I$. δ is a constant over the wavelength range of our experiments⁹. Also, depopulation of the resonant level by photoionization competes with other relaxation processes, so the linewidth has an extra intensity dependent term and becomes $\Gamma + \Gamma' I$.⁹ Therefore the rate expression becomes,

$$\text{Rate} \propto \frac{I^5 (\Gamma + \Gamma' I)}{(\Delta\omega + \delta I)^2 + (\Gamma + \Gamma' I)^2/4}$$

This rate can be numerically integrated over the time and space evolution of the intensity to give an experimental spectrum (total ions versus $\Delta\omega$), and one can thereby account for the effect of such intensity dependence on the spectrum. However this model applies only if the shot to shot intensity distribution of the laser is a very narrow spread about one intensity. The spectral effects caused by a change in spread of intensity maxima is illustrated in figure 3. Figure 3(a) shows the 4f region of the spectrum taken when the pump laser produced detectable single mode pulses 90% of the time. Dye laser pulses thus pumped had smoothly varying time evolution and a narrow spread of intensity maxima. The other 10% of the pumping pulses were multimode, and these produced highly structured dye laser pulses resulting in large single pulse excursions of the ionization signal. The four levels in the spectrum are well resolved but the resonances show slightly asymmetric lineshapes considerably broader than that expected from the laser linewidth. If this broadening is due mainly to the intensity dependent linewidth, we can estimate the coefficient, Γ' , to be about 1 cm^{-1} per 10^9 W/cm^2 .

Figure 3(b) shows the same region taken with all multimode pump pulses of the same energy per pulse as figure 3(a). In addition to a more highly structured time evolution, the dye laser pulses also have a greater spread in the distribution of intensity maxima. The resolution of the levels has degraded significantly, so that now two broad, highly asymmetric lines have replaced the four well resolved transitions. The asymmetry reflects the pulse height distribution of the laser; there are now many more pulses with intensity maxima considerably different from the average value. Sensitivity, therefore, cannot be arbitrarily

increased by merely increasing the average energy per pulse at a constant pulse length. Even for pulses with a narrow peak intensity distribution the resonances will shift and broaden, diluting the ionization strength at the maximum in addition to reducing spectral selectivity.

This problem can be solved by reducing the order of the nonlinear process or by increasing many-fold the laser pulse length. The former solution is based on the fact that four-photon ionization with a three-photon resonance or threephoton ionization with a two-photon resonance require considerably less intensity [i.e., have greater intrinsic ionization strength], which in turn decreases the affect of the intensity dependent shift and width even if the coefficients for these phenomena do not decrease. The pulse height distribution of the laser will not be significant in this case, except to scale the numerator of the ionization rate on a shot by shot basis. On the other hand, if one could lengthen the pulse at a constant intensity, the ionization fraction would increase linearly with time whereas the intensity dependent effects would be constant. Thus the width and shift would be constant and sensitivity would increase.

Double Resonance MIS of Molecular Species

We have illustrated, in the preceding sections, the utility of MIS as an analytical tool for measuring densities of atoms. Because atomic spectra are characterized by strong, sharp resonance lines in a sparse spectrum, MIS can be very selective by simply tuning the laser to an appropriate atomic resonance specific to the element one wishes to detect. By contrast, molecular spectra consist of orders-of-magnitude more lines due to their added rotational and vibrational degrees of

freedom. These additional lines make analytical measurements a nightmare for the electronic spectroscopist (whether using MIS or conventional UV absorption spectroscopy) because of the complications and interferences that arise when the spectra of different molecules overlap each other. However, this multitude of rotational and vibrational lines also provides us with "fingerprint" spectra in the infrared (IR) that can uniquely identify complicated molecules, elucidate molecular structure, and even differentiate between isotopically substituted molecules. Unfortunately, although IR spectroscopy can be very selective and discriminating, it is not particularly sensitive.

We have recently invented and developed a technique which combines the selectivity possible in the infrared with the ultimate sensitivity achievable using MIS. The concept is similar to the multiple resonance scheme shown in Fig. 1c, except that the first resonance is a molecular vibrational-rotational transition excited by a tunable IR laser. A visible laser is then tuned to a second resonance, an electronically excited state, which is subsequently ionized in the visible laser field. It is thus possible, as shown in Fig. 4, to obtain an infrared spectrum by detecting ions while the IR laser wavelength is scanned. Figure 4 immediately illustrates the utility of this technique. The upper spectrum is the IR transmission through our sample cell. In addition to the absorption lines of the NO, that we wished to detect, there are also several strong absorptions due to H₂O present. The lower spectrum shows the ionization signal during the IR scan, with the visible laser fixed on a particular NO ($^2\Pi$, $v = 1$) $\rightarrow$ ($^2\Sigma$, $v = 0$) two-photon resonance (~ 473 nm). Note that because the visible laser has been tuned to an NO resonance, only the NO is detected in the IR

scan, with no interference from H_2O .

We believe strongly that the above visible-IR double resonance technique will greatly enhance the selectivity, and thus the utility, of MIS as applied to molecular measurements. In particular, the technique looks extremely attractive for measurement of isotopically substituted small molecules because of the increased selectivity provided by the IR resonance.

Conclusion and Proposal for Phase Two Studies

We have surveyed a large region of the five-photon-ionization spectrum of xenon with four photon resonances using multiphoton ionization spectroscopy as a demonstration of a proposed technique for detecting volatile fission products. Although the high order of nonlinearity makes this an unfavorable case in many respects, we have seen a number of resonances, the strongest of which promises high sensitivity (partial pressure 0.3×10^{-6} torr) at reasonably narrow linewidth (2 cm^{-1}) for a modest input power. The sensitivity does not show the expected [intensity]⁵ scaling, due to the complications of intensity dependent linewidth and energy shift.

We propose to pursue MIS as a technique for quantitative detection of volatile fission products by extending this work to lower-order multiphoton ionizations of xenon which require less intensity. Lower order MIS will be less affected by intensity dependent widths than those transitions we have reported here and will therefore give greater sensitivity with increased selectivity. In our proposed work, we will first scan the four photon ionization with a three-photon resonance at the odd levels of 5d, since these are the lowest members of the Rydberg series and hence will have the greatest ionization strengths. This approach is preferred over the alternative, that of lengthening the laser pulse,

which is difficult to do and which gives only a linear increase in the ionization fraction. On the other hand, at lower orders, the sensitivity is still nonlinear in the intensity, an easily varied parameter, while the consequences of nonlinear side effects decrease.

We also propose to continue our measurements of molecular MIS using our new double-resonance techniques. Extension of the technique to particular isotopic species, such as $^{14}\text{CO}_2$, are of considerable interest; however, since no multiphoton ionization spectra of CO_2 have as yet been published, estimates for sensitivity limits for this case cannot be made without further laboratory experiments.

Acknowledgments

We would like to thank A. W. Johnson for helpful discussions. We also would like to gratefully acknowledge the expert technical assistance of S. A. Palmer and J. W. Clements.

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<u>Orbital Designation</u>	<u>Angular Momentum</u>	<u>State Energy (cm⁻¹)</u>	<u>Four Photon Wavelength(nm, air)</u>	<u>Relative Strength</u>
6p	1/2; 0	89860.5	445.01	.05
	3/2; 2	89162.9	448.50	.015
7p	1/2; 0	88842.8	450.12	.4
	3/2; 2	88687.0	450.91	.15
	5/2; 2	88352.2	452.62	1
4f	3/2; 2	90850.0	440.17	.5
	9/2; 4	90862.0	440.11	1
	5/2; 2	90910.6	439.87	1
	7/2; 4	90940.6	439.71	.3
8p	1/2; 0	92555.7	432.06	.1
	3/2; 2	92371.4	432.92	.08
	5/2; 2	92221.9	433.62	.03
5f	Expect 4 lines. Not resolved.	93363.2 to 93421.4	428.32 to 428.05	.2
9p	1/2; 0	94286.0	424.13	.1
	3/2; 2	94190.8	424.55	.03
	5/2; 2	94110.7	424.92	.03
6f	Expect 4 lines. Not resolved.	94735.4 to 94770.0	422.11 to 421.97	.2

Figure - 1. Multiphoton Ionization Excitation Pathways

Figure 2. APPARATUS FOR MULTIPHOTON IONIZATION SPECTROSCOPY

Figure 3. Multiphoton Ionization Spectrum of Xenon 4f States

FIGURE 4. DOUBLE RESONANCE IONIZATION OF NITRIC OXIDE

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