ULTRASLOW ATOMS AND MOLECULES GENERATED BY PHOTODISSOCIATION: METHOD AND EXPERIMENTS

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ABSTRACT

The photodissociation of molecules in a hypersonic molecular beam can yield photofragments that are moving very slowly in the laboratory frame of reference if the dissociations occur at the instant when the molecular axes are along the direction of the beam. This is the basis for a method (Zorn, 1984) of producing a sample of ultraslow atoms and molecules that can be loaded into a trap. The method, applicable to a wide variety of atoms and small molecules, concentrates the production of ultraslow photofragments in a well-defined region of the apparatus; it can be extended to produce ultraslow atoms/molecules of several different species simultaneously.   Estimates suggest that a sample of 10^5 atoms having velocities less than 5 m/sec can be produced within a 1/20 cc volume by a single, 10 mJ pulse of visible or near-ultraviolet radiation. The availability of ultraslow, neutral species makes possible an entire range of diverse experiments: *inter alia* we propose

(A)   A new method for the absolute measurement of atomic dipole polarizabilities.

(B)   A new, sensitive method for setting microscopic limits on the electron-proton charge equality.

(C)   An electro-gravitational trap for ultraslow polar molecules.

(D)   The employment of that trap as the basis of a new form of high resolution spectrometer.

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* Most of the principles discussed here apply to the production of ultraslow molecules as well as ultraslow atoms. I will occasionally emphasize this by using "atoms and molecules" in the text, but for ease in reading I often write just "atoms" for the discussion of principles except where molecular properties are essential to the arguments.

1. Introduction and General Principles

1. 1 Limitations on the slowing of a beam of atoms by radiation pressure

A significant fraction of an atomic beam can be stopped, and indeed reversed in direction, if a beam of resonance radiation shines against the oncoming atoms, but the method has well-recognized limitations:

A. The absorption frequency of fast moving atoms differs appreciably from that of the slower atoms in the beam because of the first-order Doppler shift. Thus special efforts must be made to keep the laser tuned to the peak of the absorption of the atoms being slowed.

B. The reliance on resonance radiation effectively limits experiments to those species having ground states with strong absorption lines in that portion of the spectrum where strong, tunable CW lasers are available.

C. The method as used in atoms will not work for molecules because a given molecule, with its many rotational and vibrational levels, will not stay on resonance with a predictable wavelength as a series of absorptions are followed by spontaneous radiative decays.

D. The atom to be slowed needs to absorb tens of thousands of photons, and because each radiative transition takes 10 nanoseconds or so, the stopping distance for the atom is fifty centimeters or more. To load a trap, then, requires that the tuning and timing of the laser radiation be carefully controlled so that zero velocity is achieved in just the right location.

E. The atom being slowed acquires transverse momentum as photons are spontaneously emitted in all directions, so the beam tends to bloom along x and y as it slows down along z.

F. The resonance radiation used for slowing the beam is usually quite near to the wavelength that one would like to use for interrogation of the slow atom sample, so one must turn off the momentum transfer radiation when experiments on the slow atoms are to be done.

So one can see the need and utility for a slow atom source that has the potential for being simpler and more versatile than the sources tried so far.

1.2 2. A Novel Source for Slow Neutrals: Photodissociation of Molecules

The present research follows a proposal (Zorn, 1984a) for producing a sample of slow atoms by photodissociation of the molecules in a hypersonic beam. The method is relatively simple, it is applicable in principle to any atomic species, and it is relatively unaffected by the limitations associated with the resonance radiation method. Moreover it can be generalized to work simultaneously on several different atomic species, and it can produce samples of slow molecules as well.

The experiment is one in which a fast acting valve permits a burst of molecules to enter a high vacuum chamber; the molecules are then dissociated by a short pulse of radiation from a laser. The fragments from the dissociation of any particular molecule go out along a direction determined by the orientation of the internuclear axis at the time of dissociation. Some of the molecules will dissociate at the instant when their internuclear axes are parallel to the direction of the molecular beam, and half of the fragments from these dissociations will have momenta directed antiparallel to the parent molecule's original velocity. If the type of molecule, the conditions of the beam source , and the wavelength of the dissociating radiation are chosen appropriately, a significant number of these fragments will be essentially at rest in the laboratory frame of reference; these comprise the sample of interest that will remain in the neighborhood while the faster-moving fragments and the undissociated target molecules leave.

The original considerations of this method in 1984 assumed that the fragments arising from photodissociation would have an extremely wide angular distribution; only a tiny fraction of the photofragments would be going in the desired direction. But recent work of Bucksbaum and his colleagues has showed that shaping the optical pulses provides considerable control over the direction of outgoing fragments, This may provide a way to enhance the overall efficiency of this method of generating a sample of ultraslow atoms.

The dissociation process described above can occur in a well-defined volume (dimensions on the order of 1 mm) that could be located within the electrodes/poles of the trap structure. The slow atoms can be detected by resonance fluorescence, by resonant multiphoton ionization, or other methods.

## 1.3 Novel Experiments with Ultraslow Atoms and Molecules

We propose to work on the development and execution of several experiments that are described in the following sections of this document:

(A) a new and more accurate method for the measurement of atomic dipole polarizabilities,

(B) a new and more sensitive method for setting microscopic limits on the electron-proton charge equality,

(C) an electrogravitational trap for neutral, polar molecules, and

(D) a new form of ultrahigh-resolution spectrometer for polar molecules.

2. Principles of the Method

2.1 Dynamics of Photodissociation

The potential energy diagram for a diatomic molecule is shown schematically in the figure.   The ground electronic state X has binding energy D; the excited state A goes to ground state atoms in the limit of large internuclear separation R; the excited electronic state B corresponds in that limit to one excited atom and one ground state atom.
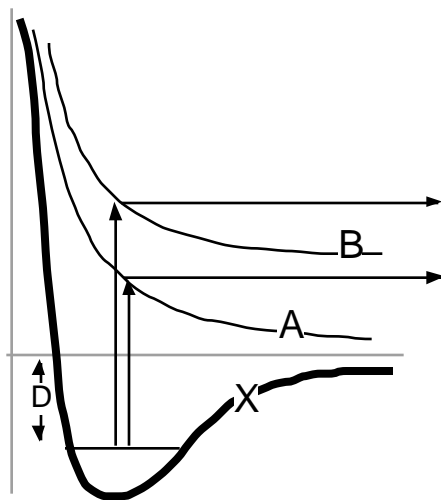
The Franck-Condon principle assures us that electronic transitions tend to occur without major changes in R, and the shaded portions of the figure show these favored regions. Dissociation results if the transition leaves the molecule on a repulsive portion of the excited state curve that is above the asymptotic energy of the separated atom state. And predissociation can occur if an excited molecular state such as C mixes with another state like B that has

a low asymptotic energy. In either case, the photon energy not used for dissociating the ground state molecule shows up in the potential or kinetic energy of the departing photofragments atoms. So if one knows the final states (i.e. the asymptotic potential energies) of the atoms, a measurement of their asymptotic kinetic energies reveals details of the dissociating state's potential energy curve.

2.2 Detection of slow fragment atoms

With the primary beam of target molecules being pulsed, the interaction region will be free of both targets and fast dissociation fragments very soon after t=0; only ultraslow atoms and residual gas molecules will remain. To verify that the dissociation process has left some fragments at rest, the interaction region will be probed with a fast and sensitive detector, highly specific for the atomic species of interest, several microseconds after the pulse of dissociation radiation has established a zero of time.

The response of the detector of ultraslow atom must be rapid enough to permit measurements of the density of the atomic sample as a function of time after the dissociation radiation shuts off. The detector must have good sensitivity because the samples will not be dense, and it must be quite specific for the atom of interest because even the best of care will not eliminate background gas from the vacuum system.

We have had good success by using a time-of-flight (TOF) mass spectrometer on ions that have been produced by resonant multiphoton ionization (RMPI) from the atoms of interest   The TOF-RMPI method has an efficiency on the order of 0.1% that depends to a considerable extent on the atomic species and on the available laser power. It would also be possible to detect the slow atoms in the sample by time-resolved resonance fluorescence, but the RMPI method seems more promising because it is applicable to a far wider range of species.

2.3 Criteria for the Choice of Molecule

The molecule of choice should dissociate to a repulsive state which gives fragments of the appropriate center-of-mass kinetic energy so that the backward-recoiling fragments will not be going too fast in the laboratory frame of reference.   Some help is to be had by selective excitation of particular dissociating states; additional adjustment can be made on the velocity of the beam molecules by varying the source temperature and pressure and by using seeding techniques.   The phase space for production of

slow fragments can be increased by making appropriate choices of mass ratio and of dissociating state.

In this experiment, a beam of molecules (ABC) is exposed to radiation to produce dissociation products AB and C. To avoid the need for special source techniques and to permit the use of a beam pulse valve, the molecule ABC should have a reasonable vapor pressure at ordinary laboratory temperatures and it should not be too reactive. It is very helpful in reducing unwanted signals if the primary beam (composed of ABC + X + Y + ...) does not have the dissociated species of interest (C or AB) as one of its components before it is exposed to the dissociation radiation. Sorting the beam with deflection fields may be   of help in attaining this when using beams of alkali dimers or jet sources for van der Waals molecules.

One needs to choose a molecule that can be efficiently dissociated with an available light source. One also needs to monitor the behavior of the resultant photofragments with a sensitive and fast-responding method. These requirements for dissociating and monitoring offer no limitation in principle to the choice of a molecule since single and multiple quantum photoexcitation/ dissociation/ionization are well understood, and since high power light sources exist for virtually every wavelength; the real constraint is the local availability of suitable lasers.

3 Advantages of the Photodissociation Source for Slow Atoms

Molecular photodissociation is a simple yet versatile approach to the production of ultra slow atoms that promises many advantages:

3.1 Applicable To Any Species:

 With the proposed method it is possible to produce a slow population of any desired atom (or, indeed, small molecule) since it is almost always possible to find the species of interest as a component of a molecule that can be photodissociated. Photofragment spectroscopy of strongly-bound molecules has been done for many years , and less stable species have also been the subject of much study. In recent years one has seen successful beam experiments with highly refractory species (e.g. tungsten and molybdenum) being seeded into a carrier gas, and with organometallic molecules containing atoms such as aluminum, gallium and indium . And the extensive work with van der Waals molecules formed in hypersonic jets shows that one can assemble almost any collection of atoms into a weakly-bound molecule: even helium can be bound to other species under jet beam conditions, so   the

production of a sample of isolated, ultraslow helium atoms is a definite possibility. And recent the results on hydrogen cluster formation suggest that ultraslow hydrogen atoms can also be generated by the   photodissociation method.

3.2 Spatial Concentration Of Sample:

The slow atoms can be produced by irradiating a spatially-concentrated sample of molecules in a highly directional, pulsed beam with a single shot of a laser. Fast atoms and molecules, whether from the primary beam or the dissociation, leave the experimental region promptly so measurements can be done on the now-isolated, slow atoms. We note that these atoms are created within a small, well-defined volume which could be located within the physical structure of trap electrodes; this avoids the many problems associated with loading a trap when the slowing process extends over tens of centimeters.

3.3 Slow Molecules Possible:

The jet source provides a beam in which the target molecules, even van der Waals clusters, are in very low rotational and vibrational temperatures; the population is concentrated in just a few quantum states, so radiation from the laser can be carefully tuned to yield the dissociation products at the desired kinetic energy. This includes the production of ultra-slow molecules from the fragmentation of larger species.

3.4 Absence Of Resonance Radiation Background:

The radiation used to produce the slow fragments has a wavelength chosen to maximize the photodissociation process, a wavelength quite distinct from the monitoring radiation which is tuned to maximize resonance fluorescence or photoionization of the photofragments. Thus the burst of dissociation radiation should not disturb (e.g. by resonant multiphoton ionization) already-trapped ultraslow atoms; moreover simple bandpass filters can keep the intense dissociation radiation from jamming the sensitive detectors of the monitoring radiation.

3.5 Compatible With Ultra-High Vacuum

: The use of a pulsed primary beam keeps the load on pumps and cold traps at a modest level so operating pressures well below 10^{-7} torr can be maintained with economical vacuum systems. Moreover, atoms that have been stopped are not subject to continuous bombardment from faster atoms that are still streaming from the source. This is particularly important if a sample is to be

stored for long times since these atoms are inordinately vulnerable to collisions.

3.6 Simultaneous Storage Of Several Species:

There is no reason why two or more different species cannot be slowed simultaneously and then stored together. This might require the use of multiple, intersecting primary molecular beams and it might use more than a single wavelength for the photodissociations, but it could open the door to a new range of experiments, both in scattering and in the comparative study of atomic properties. For example (Zorn1984b, summarized in Sec. 5), the dipole polarizabilities of different species can be compared to high precision by measuring the ratio of their frequencies of oscillation within a trap formed by standing waves of infra-red radiation.

3.7 State-Selective Operation

The method described here can be selective with respect to the quantum states of the target molecule or the resultant photofragments by appropriate choice of the wavelength of the dissociation radiation. For example the photodissociation of N02 can produce NO fragments with an inverted vibrational state population . Moreover the experiment of Zacharias et al. (1981) yielded oxygen atoms in the ground (^{3}P) state while Morrison and Grant (1982) showed that radiation in the 425-455 nm region incident on NO_2 would yield atomic oxygen in the metastable (^{1}D) state via a two-photon dissociation.

4 Range of Possible Experiments

The range of experiments that could be done with trapped, slow atoms or molecules is quite broad. We propose to work on the development and execution of several experiments that are described in the following sections of this document:

> (A) a new and more accurate method for the measurement of atomic dipole polarizabilities,
>
> (B) a new and more sensitive method for setting microscopic limits on the electron-proton charge equality,
>
> (C) a novel, state-selective electrogravitational trap (Zorn, 1984c) for ultraslow polar molecules, and

 (D) the employment of the state-selective trap in a new form of high resolution spectrometer for polar molecules.

Experiments A and B are based on the coupling of an intense, low frequency electric field with the induced electric moments in an atom; experiments C and D are based on the coupling of a permanent electric dipole moment to quasi-static fields which are timed in an appropriate manner.

In addition, precision atomic spectroscopy is an area of obvious interest, for example in measuring lifetimes of exceedingly long lived states such as singlet D atomic oxygen which are of aeronomic importance.

Another promising area for investigation is that of the spatial orderings and condensations exhibited by an ensemble of atoms in a trap or in an optical lattice under conditions where the thermal motions do not mask the effects of the very long range forces.

It might also be possible to generalize the method by ablating the species of interest from a fast-moving microsphere or inkjet droplet.

Success in generating a sample of ultraslow polar molecules would open the door to doing many experiments with Stark traps: What sort of trapping can be done within a linear multipole field if the ends of the field are closed off (perhaps gated in time?) with additional fields? These additional "end cap" fields might be generated with extra turns of wire for Zeeman traps, or with an on-axis needle at high potential in the case of a Stark trap. The theory of motion and cooling within such traps is in itself a challenging research problem.

5. Dipole Polarizabilities Measured By Wavelength Determinations Alone

The dipole polarizability ( ) of an atom is a measure of how easily its electronic structure is altered by the application of an external electric field. Its value is almost a constant provided that the time variations of the external field are slow compared to the characteristic resonance frequencies of the atom.   Its value can be related to the manner in which the atom interacts with other atoms (as in collisions or in the formation of molecular bonds). It can also be related to the manner in which the atom interacts with high frequency fields.

Polarizabilities are significant for atomic theorists in a variety of way s. For example, calculations of the polarizability are particularly sensitive to the outer reaches of the wave function because the expression for the induced

dipole moment weights the charge distribution by its distance from the origin; this contrasts to calculations of the energy which are governed by behaviors in the region where the wave function is most dense.

Previous direct determinations of atomic polarizabilities have been done by measurements of the deflection of an atomic beam ; indirect determinations have been made by interpretation of oscillator strength or lifetime measurements. These previous determinations, whether direct or indirect, are limited in accuracy to 5% at best because they require absolute calibrations of field strengths, interpretations of atomic beam deflection patterns, and careful measurements of apparatus geometry.

The 5% accuracy limit applies to the comparison of polarizabilities of two species (Crosby and Zorn, 1977) as well as for absolute determination of the polarizability of a single species. The method described here, by contrast, obtains the atomic polarizability from measurements of the wavelengths (or frequencies) of radiation that couples to the atom of interest.

Suppose we place a neutral atom in a region where there is a strong standing wave whose oscillation frequency is in the infrared, well below any of the characteristic electronic frequencies of the atom. The center of mass of the atom will oscillate in a manner governed by the coupling of the IR field and its gradients to the electric moments of the atom. The nature of that motion can be discerned by examining the spectrum of the optical resonance radiation scattered from the atom.

The coupling of the field gradient to the induced dipole moment leads to simple harmonic motion at a frequency proportional to the square root of the atomic polarizability, and by the wavelength and amplitude (but not the frequency) of the IR radiation. Here we use a low-frequency approximation to show that an absolute determination of the polarizability can be made from a measurement of the frequency of that motion provided that the amplitude of the standing wave is known [as, for example, from spectral measurements if the Stark effect of a standard molecule were used for determination of the field strength]. Even if that field amplitude is not well known, however, the atomic polarizabilities of several different species can be compared to unprecedented precision by having those species present simultaneously in the standing wave region.

This method of determining polarizabilities can be based entirely on the measurements of frequencies and wavelengths. This is in dramatic and advantageous contrast with the previous methods which depend on careful measurements of small distances (e.g. electrode spacings and atomic beam deflections), DC voltages, magnetic field strengths, and atomic velocity distributions.

6. A Test Of The Absolute Neutrality Of Un-Ionized Matter By Measurements Done At Optical Frequencies

6.1 Motivation

The physical consequences of a possible minute difference between the electron and proton charge magnitudes has been considered by physicists for many years. Since direct measurements of the electric charge on any particle or ion are limited to less than 6-place accuracy, more precise tests of charge equality (for example comparisons of lepton and baryon charges) are done by looking for a net charge on an obstensibly neutral atom or collection of neutral atoms. Such experiments have been stimulated by conjectures about the source of magnetism of the earth and by speculations about the mechanism responsible for the expansion of the universe ; these exepriments showed that the charge difference is less than 1 part in 10^{20}.

The continuing search for the fundamental bases of conservation laws and the search for unpaired quarks sustains our interest in the detection of minute charges in un-ionized matter. It is thus worthwhile to explore such methods as may offer economical promise of increased sensitivity.

6.2 Limitations to Tests for Neutrality of Matter

One important limitation to all previous tests for the absolute neutrality of un-ionized matter arises from long-term drifts in experimental parameters. The previous tests were done by setting an upper limit to the correlation of a charge-related signal with changes of a system variable: One looked for the deflection of a galvanometer as a mass of de-ionized gas left confinement; one looked for the deflection of an atomic beam, oil droplet, or suspended sphere as high voltage was connected to deflection electrodes. Because the variables could only be changed slowly, these earlier measurements were severely limited by 1/f noise and experimenters tended to take data when the apparatus "seemed to be quiet". The subjectivity inherent in this procedure, however, meant that there was no real possibility of making major improvements in results by averaging the data over several dozen runs of the experiment.

In an experiment that overcame some of these limitations, Dylla and King (1972) applied an alternating electric field to SF_6 gas that was confined within an acoustic cavity; in this situation the presence of a minute charge on each molecule would lead to the generation of a sound wave at the driving frequency.   In this way they moved the charge difference signal from below 1 Hz into the audio range above 100 Hz. and it was noted that obvious modifications to the experiment would increase its sensitivity by a factor of 1000 or more.

6.3 Testing for Minute Charges with Measurements at Optical Frequencies

I suggest that it is possible to test for the presence of minute charges on individual atoms by observing the coupling of those charges with the intense electric field produced by a focused CO_2 laser. The motion of an atom subjected to an intense standing wave of infra-red radiation (a high frequency, but still far below any resonance associated with an electronic transition in a ground state atom) will be governed by the coupling of the IR field and its gradients to the electric moments of the atom. In particular: The coupling of the field to the induced atomic dipole moment leads to simple harmonic motion of the atom. The frequency of this motion is governed by the amplitude and gradient of the IR radiation and by the polarizability of the atom; it does not depend directly on the IR frequency.

The coupling of the IR field with the atom's net charge will yield a periodic motion of the atom at the IR frequency. If this coupling occurs while the atom is also irradiated with optical resonance radiation from a narrow-band dye laser, it will cause sidebands at the CO2 frequency away from the center of the optical line; these sidebands are the signature of the net charge of the atom. This manner of detecting modifications of the scattered radiation (best done under conditions when the Doppler effect is minimized) promises to provide many of the advantages and sensitivity enhancements of heterodyne detection.

If the CO2 laser beam is focused in the area where light scattering occurs, then the highest electric fields can be at some remove from metallic or insulating materials. This minimizes the chances for high voltage breakdown which so often has limited charge equality experiments to fields of less than 10^7 V/m.

With the capacity for storing individual neutral atoms along with the availability of high electric fields at IR frequencies from a CO_2 laser, it seems quite possible to make a major advances against the previous limitations of field strength and 1/f noise in the microscopic test for the absolute neutrality of un-ionized matter.

7. Electro-Gravitational Trap And Ultra-High Resolution Spectrometer For Neutral, Polar Molecules

7.1 Principles of the Electrogravitational Trap for Neutrals

In contrast to simply-polarizable systems that are always drawn into the region of strongest electric field, a rotating (J>0) polar molecule always has some states (those with zero or low values of M_j) that exhibit a positive Stark effect in weak or moderate electric fields; molecules in those states seek regions of weak field. This can be combined with the force of gravity on the molecule to construct a trap for the long-term confinement of polar molecules.

An axially-symmetric upward force that decreases with elevation can be provided for $M_j << J$ molecules by a simple electrode such as an equipotential ring in a horizontal plane. Axial confinement can be provided from the Stark effect for provided by a set of vertical rods, of alternating polarities, spaced equally along a vertical cylindrical surface that has a diameter somewhat larger than the ring. Then, since gravity provides a uniform downward force, a position of stable equilibrium can be found for these molecules.

The electric field created by the ring alone has equipotentials that are symmetric about the ring axis. An equipotential close to the ring will be in the form of a torus; equipotentials farther away from the ring will have a saucer shape near to the axis.   It can be shown that a molecule with positive Stark Effect placed near to the axis but displaced slightly upward from the plane of the ring experiences a radial force toward the axis and a vertical force along the axis upward, away from the ring.

 Since gravity exerts its force downward, there is an on-axis position of equilibrium that is stable against substantial displacments of the molecule.

In this context we note that the experiment depends on being able to produce a reasonable number of ultra-slow polar molecules in well-defined region of the apparatus. The band structure of molecular spectra makes slowing with resonance radiation impractical for this task, but the photodissociation method is suitable.

7.2 The Basis of a High Resolution Spectrometer

We note that the trap, as described, is state-selective because the effective dipole moment of a molecule depends on its quantum state J,Mj.   Only molecules in states with a positive Stark effect can be trapped, and even stored molecules will tend to be spatially segregated within the trap according to their quantum states. Moreover, by monitoring the population of the trap it is possible to detect the occurrence of molecular transitions between trapped and a non-trapped states; this can be exploited to construct a high resolution molecular spectrometer.

If the potential on the trap ring suddenly increases, the molecules in the trapping region acquire a controllable upward velocity.   This could be used to inject the molecules with very low velocity into a homogeneous field region where radiofrequency, microwave, infrared or optical transitions could be induced.   Observation times on the order of 0.1 seconds could be expected if molecules move at about 1 meter/sec through an 0.l meter observation region.

A reflector ring above the upper aperture to the observation region would serve to return the molecules to the trap below the lower aperture.

It is the state-elective nature of the trapping that makes spectroscopy possible with this apparatus: The occurrence of radiofrequency, microwave, or optical transitions can be detected if the induced transition puts the molecule into a non-trapped state.   This is analogous to a conventional molecular beam electric resonance spectrometer but the longer transit time is expected to yield linewidths several orders of magnitude narrower than those heretofore achieved.

It seems promising to construct a spectrometer for ammonia, NH_3, for demonstration of this concept. Intense molecular beams of NH_3 that are rich in dimers have been produced, and the good vacuum needed for experiments of this sort can be attained because NH_3 is easily and efficiently pumped with liquid nitrogen cooled traps. The radiation required to photodissociate the dimers is economically available from tuned diode lasers. The Stark effect in the ground state of the NH_3 monomer is large enough so that simple electrodes at potentials no higher than 10 kilovolts are enough to impart accelerations exceeding 10^4 m/sec^2, and transitions to the non-trapped levels are in a convenient region of the microwave spectrum. The detection of NH_3 molecules, alas a more difficult task than it is for sodium, can be accomplished with resonantly-enhanced two-photon ionization.