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# Atmospheric Photo Ionization of Argon with a Short Pulse Laser

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## CONTENTS

I. INTRODUCTION .....	1
II. THE TWO LEVEL SYSTEM .....	3
III. THE MULTISTATE SYSTEM, FERMI'S GOLDEN RULE .....	4
IV. SINGLE PHOTON EXCITATION FOR ATOMS AND MOLECULES .....	5
V. SINGLE PHOTON IONIZATION .....	8
VI. MULTI PHOTON PROCESSES .....	10
VII. THE RATE EQUATIONS .....	12
VIII. SUMMARY .....	13
ACKNOWLEDGMENT .....	13
REFERENCES .....	13

# ATMOSPHERIC PHOTO IONIZATION OF ARGON WITH A SHORT PULSE LASER

## I. Introduction:

One of the goals of the NRL laser/atmosphere program is to use a short pulse laser to produce an atmospheric breakdown at a controlled distance from the laser. The currently favored way of doing this is to use the dispersive properties of the atmosphere to compress a pulse longitudinally until it gets to the irradiance where self focusing can compress it in the transverse plane [1]. The compressed pulse reaches such an irradiance that it generates breakdown in the atmosphere. Although final laser parameters are not specified at this point, as a rule of thumb, we think of a 1 ps pulse, that compresses to 100 fs as it propagates, and we think of the irradiance after self focus as being about  $10^{12} - 10^{13}$  W/cm<sup>2</sup>. Clearly to control the distance of breakdown, one must control the bandwidth of the laser; as the spread in group velocity increases, the focal point moves closer to the laser.

However the chirped, short pulse lasers typically radiate only about one Joule per pulse. Taking an ionization energy of 15eV, this can generate at most  $4 \times 10^{17}$  electron ion pairs if no laser energy is lost to other processes. Furthermore, in the atmosphere, these electrons last only a few ns due to three body attachment to oxygen. For certain applications, this may be sufficient. Other applications might require more electrons and/or longer life. For these latter applications, the photo ionized plasma could serve as a seed plasma. This seed plasma could be ionized by for instance a focused, high power CO<sub>2</sub> laser. As long as the seed electrons are present in the atmosphere, a CO<sub>2</sub> laser is ideal (right frequency, high power, high efficiency) for avalanche breakdown of the atmosphere. However the frequency of the CO<sub>2</sub> laser is far too low to generate the required seed ionization by multi-photon seed ionization (it would be more than a 100 photon process), thereby opening an opportunity for seed ionization by a much higher frequency laser.

The pulse time of this high frequency laser is too short for avalanche ionization, and the irradiance is too low for tunneling ionization. Hence one is left with multi photon ionization. The question is how to pick the laser parameters so as to optimize this process. Before we begin we briefly discuss photo ionization. If a photon has energy above the ionization energy, photo ionization usually proceeds very quickly for a high power laser. However, if its energy is below the ionization energy, two or more photons may combine coherently, or incoherently to ionize the atom. Multi-photon ionization has been a well known process for a long time [2-5]. Numerous experiments have studied it [6]. If the ionization energy is  $E_i$  and the photon energy is  $E_{ph}$ , one would naturally think that minimum number of photons required would be  $E_i/E_{ph}$ . However because of the presence of excited states below the ionization threshold, it is also possible that that fewer photons could be required because the ionization might proceed via a cascade process through one or more of these excited states. Such a process has been called resonantly enhanced multi photon ionization (REMPI). Recently this author has argued, using experimental data and simple theoretical concepts [7], that for short pulse, high power lasers, REMPI could occur quite frequently, indicating that the number of photons required could be more accurately estimated as something like  $(0.75-0.9) E_i/E_{ph}$ . This memo suggests one particular strategy to optimize REMPI in the atmosphere.

It suggests that ionizing the argon, rather than the oxygen or nitrogen could be the easiest way to generate the ionization. The atmosphere is about 78% N<sub>2</sub>, about 21% O<sub>2</sub>, and about 1% Ar.

Thus there is plenty of argon to produce a dense plasma. The ionization energy of  $O_2$  is 12.1 eV, that of  $N_2$  is 15.6 eV, and that of Ar is 15.8 eV, so one could naturally question why the argon would ever be the easiest component to ionize. The possible answer may be that argon is an atom, whereas the other two are molecules. Thus the intermediate electronic excitations of argon are isolated states, whereas the excited electronic states of the molecule occur in broad bands because of the presence of so many nearby vibrational and rotational states. As we will discuss shortly (and as is well known), the excitation of isolated states is usually a much stronger process than excitation states in a band. Thus, if the laser frequency is picked properly, one might be able to ionize the argon component of the air by exciting through this intermediate state, furthermore, this intermediate state may be easier to access than the analogous intermediate molecular state. Others have also suggested this same approach, for other applications, using both atmospheric argon [8] and xenon [9].

Let's now scope out the problem. We want the photon energy to be as high as possible, so as few photons as possible are required for the multi photon processes. However the photon must also propagate freely in the atmosphere. The shortest wavelength photon that propagates essentially loss free in the atmosphere has a wavelength of about 3750 Angstroms, or about 3.3 eV. The lowest energy electronic excitation of argon (designated  $4s[1\frac{1}{2}]^0$ ) has an energy of about 11.65 eV above the ground state (designated  $3p^6\ ^1S$ ) [10]. However this state has odd parity, opposite to the ground state's even parity. Therefore, if we consider only dipole transitions, we must consider a three photon process. However a 3.9 eV photon does not propagate long distance in the atmosphere, so we do not consider this process.

The next even state is designated  $4p[1/2]$  and has an energy of 13 eV, so it can be excited by a four photon process with a 3.25 eV photon. Then the excited state can be ionized in a single photon process, which, as we will see, goes very quickly. Hence the 4 photon excitation of argon is the rate limiting step. Since it is a resonant process, and the competing process, four photon direct ionization of  $O_2$  is not, we would expect it to go faster. Thus one could envision a cascade process. The most difficult first task is to excite the argon atom with 4 photons. Then ionizing it with a single photon is much easier.

Although we focus on the four photon excitation of the  $4p[1/2]$  state with a 3.25 eV photon, there are other possibilities as well. The  $4s[1\frac{1}{2}]^0$  state could be excited by 5 photon process with a 2.33 eV photon, followed by two photon photo ionization of the excited state. Also this state could be excited by a four photon process if one of the intermediate state matrix elements happens to be unexpectedly large for a quadrupole transition. If this occurs, it turns out that there are several other  $5p$  states just 2.9 eV above, so it could be excited by a single photon, followed by single photon excitation.

To quantify this theoretically however, one would have to do multi photon quantum mechanical perturbation calculations for many electron atoms and molecules. We do not attempt that here. Alternatively, one could attempt to settle it experimentally. Using a tunable high power short pulse laser (FEL? dye laser?, frequency doubled Ti:sapphire laser?), one could attempt to ionize air with photon energies around 3.25 eV and investigate whether there is a resonant process to be exploited. Furthermore one could also perform analogous experimental investigations for photon energies around 2.33 and 2.9 eV.

While the necessary theoretical calculations are difficult, one can obtain considerable insight by doing a variety of simpler quantum mechanical calculations. In fact, these simple calculations do indeed indicate that ionization via the argon channel is several orders of magnitude faster than the direct 4 photon ionization of O<sub>2</sub>. In Section II we look at two state systems, in Section III, multistate systems (Fermi's golden rule). In Section IV we look into single photon excitations of atoms and molecules and give rates for simple systems or rough approximations for more complicated ones. In Section V we look into single photon ionization, while in Section VI we look into multiphoton process for atoms and molecules. Section VII discusses solutions to the rate equations for 4 photon ionization of argon, and Section VIII summarizes.

## II. The Two Level System:

This section and the next briefly reviews quantum mechanical perturbation theory. These are rather brief, as this information can be found in the standard texts. The system is governed by Schroedinger's equation

$$i\hbar \frac{\partial \psi}{\partial t} = H\psi \quad (1)$$

where H is the Hamiltonian operator. If H were time independent, we would have

$$\psi(r, t) = \psi(r) \exp\left(-\frac{iE}{\hbar}t\right) \quad (2)$$

Let us say that in the system we consider, there are only two states, denoted by subscripts zero and one. They are orthogonal to each other and each is normalized to unity in the usual way. since the system is a two state system, these eigenfunctions are also complete. Then the wave function will always be the linear combination

$$\psi(r, t) = C_0 \psi_0(r) \exp\left(-\frac{iE_0}{\hbar}t\right) + C_1 \psi_1(r) \exp\left(-\frac{iE_1}{\hbar}t\right) \quad (3)$$

where because of the completeness,  $|C_0|^2 + |C_1|^2 = 1$ . Let us say now that there is a time dependent perturbed Hamiltonian, but this perturbation does not change the two state nature of the system. Then the solution to Schroedinger's is as written in Eq.(3), except that now, each C must be a function of time. Assuming this, and further assuming that the time dependence of the perturbation goes as  $\epsilon_0 \cos \omega t$ , we substitute into Schroedinger's equation. On the left hand side we find terms proportional to the  $\psi$ 's and their time derivatives. Also many terms cancel because the  $\psi$ 's are solutions to the time independent Schroedinger's equation. Multiplying the resulting equation by first  $\psi_0$  and integrating over space, and then  $\psi_1$ , we find two equations for the time derivatives of the C's. These are

$$\frac{dC_0}{dt} = \frac{M}{i\hbar} C_1 \exp -i\Delta\omega t \quad (4a)$$

$$\frac{dC_1}{dt} = -\frac{M^*}{i\hbar} C_0 \exp i\Delta\omega t \quad (4b)$$

where  $\hbar\Delta\omega = E_1 - E_0 - \omega$  and  $M = \langle \psi_0^* | \delta H \psi_1 \rangle = \int d^3r \psi_0^* \delta H \psi_1$ . In writing Eqs.(4a and b) we have used the Hermitian properties of  $\delta H$ . Also we assume that  $\Delta\omega$  is small (leading to secular, long time scale changes in the C's) and have thereby also dropped the higher frequency term on the right and side. Defining  $\Omega_0^2 \equiv |M|^2 / \hbar^2$ , Eqs.(4) are harmonic oscillator equations with a frequency  $\Omega$  given by

$$\Omega = \frac{\Delta\omega \pm \sqrt{\Delta\omega^2 + \Omega_0^2}}{2} \equiv \Omega_{\pm} \quad (5)$$

If  $\Delta\omega = 0$ , the perturbation causes the system to oscillate between states 0 and 1 with frequency  $\Omega$ .

### III. The Multistate System, Fermi's Golden Rule:

Let us imagine the lower state, zero still being a single state, but the upper state being one of many possible states. That is we replace the subscript 1 with j, which is now an index of summation. Equation (4b) can be integrated once to give

$$C_j = \frac{iM_j^* C_0}{\hbar} \exp i(\Delta\omega_j t / 2) \frac{\sin(\Delta\omega_j t / 2)}{\Delta\omega_j / 2} \quad (6)$$

Multiplying the equation for  $C_j$  by the equation for  $dC_j^*/dt$  and adding the complex conjugate, we find

$$\frac{d|C_j|^2}{dt} = 4\pi\Omega_{0j}^2 \delta(\Delta\omega_j) |C_0|^2 \quad (7)$$

where we have used the convention that for long time,  $\omega^{-1} \sin\omega t \rightarrow \pi\delta(\omega)$ . Of course because of the completeness, we still have  $|C_0|^2 + \sum_j |C_j|^2 = 1$ . Hence to find the loss from the original state, we sum over all j and find

$$\frac{d|C_0|^2}{dt} = -\sum_j 4\pi|\Omega_{0j} C_0|^2 \delta(\Delta\omega_j) \quad (8)$$

which is valid as long as  $|C_0|^2 \gg |C_1|^2$ . The delta function only makes sense for an integral, not a summation. To convert the summation to an integral, we need a density of states  $\rho(\omega)$ ,

$$\sum_j = \int d\omega \rho(\omega) \quad (9a)$$

and this depends on the details of the physical situation. Integrating we find

$$\frac{d|C_o|^2}{dt} = -\sum_j 4\pi |\Omega_{oj} C_o|^2 \rho(\Delta\omega_j = 0) \sim -4\pi \frac{\Omega_o^2}{\Delta\omega_B} |C_o|^2 \quad (9b)$$

where  $\Delta\omega_B$  is the frequency width of the band of states. We will denote this a molecular, as opposed to an atomic process, for reasons which will become clear shortly.

Alternatively, if the state is isolated but the laser has a spread in frequency  $\delta\omega$ , so that the irradiance  $I = \int d\omega I(\omega)$ , then the sum over  $j$  in Eq. (8) becomes an integral over  $\omega$ . If the irradiance has frequency spread  $\delta\omega$ , which is many instances is the reciprocal of the pulse time  $\tau_p$ , then the rate goes roughly as

$$\frac{d|C_o|^2}{dt} \sim -4\pi \Omega_o^2 \tau_p \quad (10)$$

We call this the rate for an atomic process since these states are isolated.

If the  $\Omega_o$  for the atomic and molecular processes are about the same, to optimize the irradiance for maximum excitation during the pulse, we set  $4\pi \Omega_o \tau_p \sim 1$  (larger irradiance will cause the excitations to oscillate during the pulse). At this irradiance, the molecular excitation rate is smaller by a rate of  $4\pi \Delta\omega_B \tau_p$ , or at least three orders of magnitude for a 1 eV band and a 100 fs pulse.

#### IV. Single Photon Excitation for Atoms and Molecules:

Here we calculate for simple systems, and estimate for more complicated systems, the single photon excitation rate. The perturbed Hamiltonian is

$$\delta H(r, t) = -e r \cdot \epsilon_o \cos \omega t \quad (11)$$

that is the energy of the displaced charge in the oscillating field. The radiation field has a spatial dependence as well, but the wavelength is normally large compared to atomic or molecular distances so we neglect it in the dipole approximation. Since in the derivation in Sections 2 and 3, the perturbed time dependence was expressed in term exponentials rather than cosines, the matrix element is  $\langle \psi_1^* | e r \cdot \epsilon \psi_o \rangle$  will have an additional factor of  $1/2$ .

IVa. Atoms: For the two states, we use the ground state and  $1P^0$  excited state for the hydrogen atom. These wave functions are



$$\psi_0 = \frac{2}{a_0^{3/2} \sqrt{4\pi}} \exp\left(-\frac{r}{a_0}\right) \quad (12a)$$

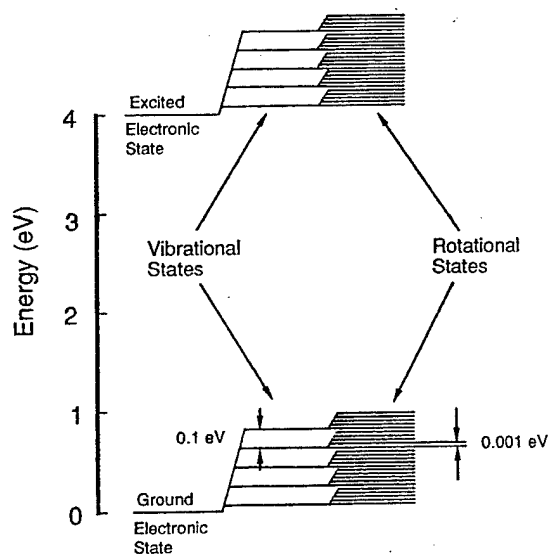
$$\psi_1 = \frac{r}{4a_0^{5/2} \sqrt{2\pi}} \exp\left(-\frac{r}{a_0}\right) \cos \theta \quad (12b)$$

where  $\theta$  is the polar angle to the z axis, defined by the direction of the electric field. The quantity  $a_0$  is the Bohr radius  $a_0 = \hbar^2/me^2$ . The integrals are all straightforward, and we find the matrix element is given by  $M = 1.6e\epsilon_0 a_0$ , and the oscillation frequency between states by

$$\Omega = \frac{1.6e\epsilon_0 a_0}{\hbar} \quad (13)$$

In cgs units, take the approximate values  $e = 5 \times 10^{-10}$ ,  $\hbar = 10^{-27}$ ,  $a_0 = 5 \times 10^{-9}$ . For the electric field we assume a canonical irradiance of  $10^{12} \text{ W/cm}^2$ . In this case,  $\epsilon = 6 \times 10^4 (I/10^{12})^{1/2}$ , so  $\Omega \approx 2.4 \times 10^{14} (I/10^{12})^{1/2}$ .

IVb. Molecules: For molecules, the excited states are not isolated as they are in an atom. Rather they occur in bands because for each electronic excitation, there are a very large number of vibrational and rotational state states as well. Schematically, the electronic excitations are sketched below as:





## V. Single Photon Ionization:

Here we do not distinguish between ionization of atoms and molecules, because in each case, the final state is similar, a free electron. If the free electron has high energy compared to the ionization energy, it is not strongly affected by the nucleus. We assume that in this case, the electron is a freely propagating wave. If it is in a box of size  $L$  on a side, the wave function for the free state is  $L^{-3/2} \exp i\mathbf{k}\cdot\mathbf{r}$  in the high energy limit. Then the matrix element is given by

$$M(\mathbf{k}) = \frac{1}{2\sqrt{\pi}(a_0L)^{3/2}} \iiint d^3r \epsilon_0 \cdot \mathbf{r} \exp[i\mathbf{k}\cdot\mathbf{r} - r/a_0] + \text{c.c.} \quad (14)$$

where again,  $\epsilon_0$  is the amplitude of the electric field expressed as a cosine. Now say  $\theta$  is the angle between  $\epsilon$  and  $\mathbf{k}$ ,  $\theta''$  is the angle between  $\mathbf{r}$  and  $\epsilon$ , and  $\theta'$  is the angle between  $\mathbf{r}$  and  $\mathbf{k}$ . If we let  $\mathbf{k}$  be the polar axis, then we can relate  $\theta''$  to the other angles  $\cos\theta'' = \cos\theta' \cos\theta + \sin\theta' \sin\theta \cos(\phi' - \chi)$  where  $\phi'$  and  $\chi$  are the azimuthal angles. The volume element is then  $r^2 dr \sin\theta' d\theta' d\phi$ . The integrals over  $\phi'$  vanish, so we are left with

$$\begin{aligned} M(\mathbf{k}) &= \frac{\pi}{\sqrt{\pi}(a_0L)^{3/2}} \iint r^2 dr \sin\theta' d\theta' \epsilon_0 r \cos\theta \cos\theta' \exp[ikr \cos\theta' - r/a_0] + \text{c.c.} \\ &= \frac{16\pi\epsilon_0 k a_0^5 \cos\theta}{(\pi a_0^3 L^3)^{1/2} (1 + k^2 a_0^2)^3} \end{aligned}$$

To get the ionization rate, we use the golden rule, Eq (8). To do so we need the density of states. The energy of an electron with wave number  $k$  is  $E_k = \hbar^2 k^2 / 2m$ , so the density of states with energy  $E_k$  is

$$\rho(E_k) = \frac{L^3 m^{3/2} \sqrt{E_k}}{\sqrt{2\pi^2 \hbar^3}} dE_k$$

Using the relation between energy and frequency, we can do the integral in Eq. (8) to get the ionization rate  $w$ ,

$$w = \frac{256mk^3 e^2 \epsilon_0^2 a_0^7}{3\hbar^3 (1 + k^2 a_0^2)^6} \quad (15)$$

where we have integrated over angle. Of course  $k$  is related to the photon energy and ground state energy  $E_0$  (a negative number by)  $\hbar^2 k^2 / 2m = \hbar\omega + E_0$ . As a function of  $k$ ,  $w$  in Eq. (15) has a maximum at  $ka_0 = 1$ , at which point, we find  $w \sim 10^{12} \text{ s}^{-1}$  for our canonical irradiance of  $10^{12} \text{ W/cm}^2$ . For larger  $k$ , the rate falls off rapidly with photon energy.

Equation 15 also shows that at threshold,  $k \rightarrow 0$ , the rate rapidly goes to zero. This is not the correct behavior, and it arises from the assumption of a freely propagating electron wave. Near zero energy, the electron wave function is strongly affected by the nucleus. The calculations of ionization rate near the absorption edge are difficult [12]. To get an approximate value, we assume that the matrix element and state density do not change very much on going just below to just above the ionization energy. This is rather like the orbits of particles near the separatrix in a sinusoidal potential. Other than the fact that the just barely trapped orbits are confined and the just barely untrapped orbits are not, the nature of the orbits are very similar along any nearly portion of the orbit.

Hence we approximate the ionization rate with the transition rate to very high Rydberg states in the atom. Since the ground state has  $l=0$ , the only allowed dipole transitions are to  $l=1$  states. In terms of the ionization energy  $E_i \equiv \hbar\omega_i$ , the energy of a Rydberg state of quantum  $n$  is  $-E_i/n^2$ . If the radial part of the wave function is  $R(r)$ , Schroedinger's equation for  $R$  becomes

$$-\frac{1}{r^2} \frac{d}{dr} r^2 \frac{dR}{dr} = -\frac{2}{n^2 a_0^2} R + \frac{2}{a_0 r} R - \frac{2}{r^2} R \quad (16)$$

where we assume  $n$  is large. For large  $r$ , the angular momentum barrier (last term on rhs) plays almost no role, and for small  $r$ , the energy eigenvalue (the first term on rhs) plays almost no role. If one uses a WKB approximation for  $R$ , the function is oscillatory in  $r$  as long as  $a_0 < r < n^2 a_0$ , and it exponentially damps away for larger  $r$  (the eigenvalue is selected to eliminate the exponentially growing solution). Thus for  $r < n^2 a_0$ , the magnitude of  $R$  is roughly uniform, so that the normalization for the wave function is roughly  $R \sim 1/(a_0^{3/2} n^3)$ . The value of the radial part of the ground state is given in Eq. (10a). so the matrix element is given roughly by  $M \sim e\epsilon_0 a_0 / n^{3/2}$ . The ionization rate is given by Eq. (8), which is roughly

$$w \approx 4\pi\omega_i \frac{[e\epsilon_0 a_0]^2}{E_i^2} \quad (17)$$

where we have used for the density of states for high Rydberg states

$$\frac{dn(\omega)}{d\omega} = \frac{1}{2} \sqrt{\frac{\omega_i}{\omega^3}} = \frac{n^3}{2\omega_i}$$

If the initial state were not the ground state, but a higher Rydberg state with principle quantum number  $n_0$ , an analogous argument shows that the matrix element is multiplied by  $n_0^3$  and the rate goes roughly as

$$w \approx 4\pi\omega_i n_0^6 \frac{[e\epsilon_0 a_0]^2}{E_i^2} \quad (17a)$$

Notice that at threshold, the rate no longer vanishes, as the high energy approximation, Eq. (15) would have predicted. Instead, at threshold, one has an ionization rate given roughly by Eq. (17).

As the photon energy increases, the rate decreases, ultimately being given by the high energy approximation, Eq. (15). Expressing the rate in terms of an ionization cross section,  $w = \sigma_i[I/\hbar\omega_i]$ , and expressing the irradiance as  $I = c\epsilon_0^2/8\pi$ , we find near the ionization threshold,

$$\sigma_i \approx 32\pi^2 \left( \frac{e^2}{\hbar c} \right) a_0^2 \quad \text{or} \quad \sigma_i \approx 32\pi^2 n_0^6 \left( \frac{e^2}{\hbar c} \right) a_0^2 \quad (17b)$$

the latter being for an excited state. For the ground state, we find  $\sigma_i \sim 5 \times 10^{-17} \text{ cm}^2$ , about the right value. Thus approximating the wave function for energy just above zero, with that for energy just below zero gives a simple and reasonably accurate estimate of the ionization cross section, or ionization rate, just above threshold.

## VI. Multi Photon Processes:

Multi photon processes are extremely complicated to calculate, even for a hydrogen atom, so we will confine ourselves to their rather general properties. We find that if the levels are isolated, as in an atom, there are still oscillations between the states. While the process is nonlinear in the matrix element (i.e. in  $\epsilon$ ), it is still linear in the two states, zero and one, which are connected by the multi photon process. On the other hand, if the final state is a band of states (or ionization), the basic behavior is again as in the case of single photon excitation. That is there is an analog to the golden rule, but the coefficient now goes as some higher, but even power of  $\epsilon$ . For multi photon processes, it now becomes essential to consider other excited states. We will define by zero and one the two isolated states we expect to connect with a multi photon process and consider other states as well with an index  $j$  which goes from 2 to some upper limit  $P$ . The  $P+2$  eigenfunctions once more are assumed to form a complete orthonormal set. Then Eqs 4 become

$$\frac{dC_0}{dt} = \frac{M_{01}}{i\hbar} C_1 \exp(-i\Delta\omega_{01}t) + \sum_{j=2}^P \frac{M_{0j}}{i\hbar} C_j \exp(-i\Delta\omega_{0j}t) \quad (18a)$$

$$\frac{dC_1}{dt} = \frac{M_{10}}{i\hbar} C_0 \exp(-i\Delta\omega_{10}t) + \sum_{j=2}^P \frac{M_{1j}}{i\hbar} C_j \exp(-i\Delta\omega_{1j}t) \quad (18b)$$

$$\frac{dC_j}{dt} = \frac{M_{j0}}{i\hbar} C_0 \exp(-i\Delta\omega_{j0}t) + \frac{M_{j1}}{i\hbar} C_1 \exp(-i\Delta\omega_{j1}t) + \sum_{k \neq j}^P \frac{M_{jk}}{i\hbar} C_k \exp(-i\Delta\omega_{jk}t) \quad (18b)$$

where now the  $\Delta\omega$ 's are defined analogously, except that now  $\Delta\omega_{jk} = -\Delta\omega_{kj}$  and the matrices have the same symmetry properties as before. To illustrate the nature of the coupling, let us assume that states 0 and 1 have an energy separation close to  $2\hbar\omega$ , and assume further that only a single other state, say  $C_2$  is important for the coupling. Then integrating Eq. (18b) we find

$$C_2 = \frac{M_{20}}{\hbar\Delta\omega_{20}} C_0 \exp(-i\Delta\omega_{20}t) + \frac{M_{21}}{\hbar\Delta\omega_{21}} C_1 \exp(-i\Delta\omega_{21}t) \quad (19)$$

where in Eqs (18 and 19) the  $\Delta\omega$ 's are not small. Then we substitute for  $C_2$  on the right hand sides of Eqs (18a and b) to determine the next order equation for  $C_0$  and  $C_1$ . Then we get for  $C_1$

$$\frac{dC_1}{dt} = \frac{M_{12}M_{20}}{i\hbar^2\Delta\omega_{20}} C_0 \exp-i(\Delta\omega_{12} + \Delta\omega_{20})t \quad (20)$$

and analogously for  $C_0$ . In Eq. (20) we have kept only those exponentials which are at low frequency, that is at a frequency near  $[(E_1 - E_2)/\hbar - 2\omega] = 0$ . Equation 20 and the analogous equation for  $C_0$  are still linear in the  $C$ 's even though the coupling coefficient is now proportional to  $\epsilon^2$  rather than simply  $\epsilon$ . They are still harmonic oscillator equation equations, so the process still has the populations oscillate sinusoidally, but now at frequency  $\Omega_2 \equiv |M_{12}M_{20}/\hbar^2\Delta\omega|$ , between the two states which are connected by the two photon process. The rate for the two photon process as compared to the one photon process is given roughly by

$$\frac{\text{onephotonrate}}{\text{twophotonrate}} \sim \frac{\Omega_2}{\Omega} \sim \frac{M}{\hbar\Delta\omega} \sim \frac{\epsilon\epsilon_0}{\hbar\Delta\omega} \quad (21)$$

This ratio is proportional to the electric field  $\epsilon$ , and the rate itself is proportional to  $\epsilon^2$ .

Two photon processes (and even more emphatically, greater than two photon processes) are not as constrained by selection rules as are single photon processes. For instance, states zero and one may be forbidden dipole transitions. However each may have a non zero matrix element between itself and state two, and there are many possible intermediate states. Thus usually we would expect a multiphoton path between the two states. For more than two photon processes, there are even more channels. Nevertheless, if only dipole transitions are considered, odd to even states must be connected by odd numbers of photons, and visa versa.

If the intermediate state is a band of states rather than an isolated state, the transition rate will not be significantly different, the distinction only arises if the band is resonant or nearly resonant. However since  $\Delta\omega_{02}$  is not small, the intermediate state can be an isolated state or a band of states. But if the final state is a band of states, the result is still significantly different. Say that states zero and two are isolated (but two may be part of a band without significant effect) and one is a band of nearby states. In that case the procedure is the same as in Section 4b. We solve for  $C_1$  by integrating Eq(20) once in time. Multiply this by the complex conjugate of Eq. (20), and add the complex conjugate of the product to get an equation for the rate of change of  $|C_1|^2$ . It is

$$\frac{d|C_{1j}|^2}{dt} = 4\pi \frac{|M_{1j}M_{20}C_0|^2}{\hbar^4\Delta\omega_{20}^2} \delta\left[\frac{E_{1k} - E_0}{\hbar} - 2\omega\right] \quad (22)$$

Thus if the final state is a band of states, of bandwidth  $\Delta\omega_B$ , and all these states have about the same matrix element, we may, as for the single photon case, consider it to be a single macrostate in a frequency range  $\Delta\omega_B$ , giving a density of states  $\Delta\omega_B^{-1}$ , so that

$$\frac{d|C_1|^2}{dt} = 4\pi \frac{|M_1 M_{20} C_0|^2}{\hbar^4 \Delta\omega_{20}^2 \Delta\omega_B} \sim 4\pi \frac{\Omega_o^4}{\Delta\omega^2 \Delta\omega_B} \equiv 4\pi \frac{\Omega_2^2}{\Delta\omega_B} \quad (23)$$

Instead, if the states are isolated but the laser has bandwidth  $\delta\omega_L$ , possibly equal to  $\tau_p^{-1}$ , then

$$\frac{d|C_1|^2}{dt} \sim 4\pi\Omega_2^2\tau_p \quad (24)$$

Once again, if  $\Omega_2\tau_p \leq 1$ , the incoherent rate is not that much less than the coherent rate. If we define  $\Omega_n = \omega_L [e\epsilon a_0/E]^n$ , where  $E$  is a typical energy gap between the relevant states, then the  $n$  photon atomic excitation rate goes roughly as  $4\pi\Omega_n^2\tau_p$ . Similarly, the  $n$  photon ionization rate from the ground state, by analogy to Eq. (17), goes roughly as

$$w_n \sim 4\pi\omega_L [e\epsilon a_0/E]^{2n}. \quad (25)$$

Thus the  $n$  photon excitation rate exceeds the  $n$  photon ionization rate by a factor of  $4\pi\omega_L\tau_p$ , a factor of several orders of magnitude. This then is the principle motivation for our expectation that four photon photo excitation of the argon might be a much faster process than direct four photon ionization of  $O_2$ . The former is a resonant process, the latter is not.

## VII. The Rate Equations:

We would like to finish by writing out rate equations for the ground state, excited state and electrons. Using subscripts  $g$ ,  $x$  and  $e$ , we find

$$\frac{dn_g}{dt} = \Omega_x (n_x - n_g) \quad (26a)$$

$$\frac{dn_x}{dt} = -\Omega_x (n_x - n_g) - v_i n_x \quad (26b)$$

$$\frac{dn_e}{dt} = v_i n_x \quad (26c)$$

where  $\Omega_x$  is the four photon excitation rate for argon, and  $v_i$  is the ionization rate of the excited argon atom. Also we have included the fact that the electric field excites the atom and  $de$  excites it at the same rate. Equations give the trivial conservation law that total number of particles is conserved. We expect that  $v_i \gg \Omega_x$ , so that the excited state is quasi steady in time. Setting the left hand side of Eq. (26) to zero, we can solve  $n_x = [\Omega_x / (v_i + \Omega_x)] n_g \ll n_g$ . Hence the ionization rate is simply the excitation rate of the argon. Because it is a resonant process, we expect this rate to be much larger than the analogous ionization or excitation rates for the molecular components of the atmosphere.

## VIII. Summary.

In this memo, we have laid out the case that the optimum way to ionize the atmosphere, at a controlled range, with a short pulse, high power laser may well be to ionize the argon rather than the oxygen or nitrogen. The reason is that the argon is an atom, not a molecule. As such its electronic excitations are isolated rather than part of a band structure. If the laser is properly tuned, they should be much easier to excite. We have also laid out a possible route, a 4 photon excitation, followed by photo ionization of the excited atom. Other routes are also possible. Our rough estimate is that this rate could be greater than the direct four photon ionization of oxygen by as much as several orders of magnitude. To evaluate this more accurately, we would have to do the multi photon multi electron calculations not only for argon, but also for the oxygen molecule. That way, we could compare the two and see which is better.

An important issue is that even if we do these calculations, would we believe them? To this author they look so complicated that I would not be so sure. Of course if we do adopt such an ionization scheme, we would ultimately have to do them. However for the short or intermediate term, an alternative could be to simply do the experiment.

One possibility would be to use our own Ti:sapphire laser and frequency double it. Alternatively, at the Jefferson Lab FEL, with frequency multiplication, they could be in the optical regime, albeit at rather low power and efficiency [13]. However, within the next six months to year, they do expect to have their system operating much more efficiently in the uv and optical range. Either way, the idea would be to send the laser light into a target chamber containing only air, but possibly at reduced pressure, so that if there is ionization, the electron lifetime would be longer and easier to measure. Then we would look at the ionization as a function of frequency and irradiance. The irradiance one could probably most easily vary by changing the focal conditions of the beam. We would like to vary the photon energy between about 3 and 3.5 eV, around the upper limit of photon energy that propagates in the atmosphere, and see if there is a resonant process at a photon energy of about 3.25 eV. If so, it would indicate that four photon excitation of argon is playing the key role in the ionization process. Other photon energies which might be of interest for ionization of the argon could be 2.33 and 2.9 eV.

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