

Supplementary Information

Detection Limits of Organic Compounds Achievable with Intense, Short-Pulse Lasers

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Ionization Probabilities

Resonant Two Photon Ionization

For a molecule with an ionization potential I_p is irradiated with photons of energy $\hbar\omega$, if there is an intermediate excited state (1) at an energy $\hbar\omega$ above the ground state (0), then if $I_p < 2\hbar\omega$, the probability of these levels and the continuum (2) being populated is governed by the following rate equations assuming the lifetime of the excited state is long compared to laser pulse length

$$\frac{dP_0}{dt} = -\Gamma_1 P_0$$

$$\frac{dP_1}{dt} = \Gamma_1 P_0 - \Gamma_2 P_1$$

$$\frac{dP_2}{dt} = \Gamma_2 P_1$$

For a laser intensity I , the excitation rate from ground to excited state and ionization rate of the excited state are related to the cross sections σ for the respective processes by

$$\Gamma_1(I) = \sigma_1 \frac{I}{\hbar\omega}$$

$$\Gamma_2(I) = \sigma_2 \frac{I}{\hbar\omega}$$

Solution of the rate equations assuming I is constant and $P_0 = 1, P_1 = P_2 = 0$ at $t = 0$ are

$$P_0 = \exp(-\Gamma_1 t)$$

$$P_1 = \frac{\Gamma_1}{\Gamma_2 - \Gamma_1} [\exp(-\Gamma_1 t) - \exp(-\Gamma_2 t)]$$

$$P_2 = 1 - \frac{\Gamma_2 \Gamma_1}{\Gamma_2 - \Gamma_1} \left[\frac{1}{\Gamma_1} \exp(-\Gamma_1 t) - \frac{1}{\Gamma_2} \exp(-\Gamma_2 t) \right] \quad (\text{S1})$$

where $P_{1+1} = P_2$ is the resonant ionization probability. For low intensities where the ionization probabilities are low, expansion of the exponentials to second order gives

$$P_{1+1} = 1 - \frac{\Gamma_2 \Gamma_1}{\Gamma_2 - \Gamma_1} \left[\frac{1}{\Gamma_1} \left(1 - \Gamma_1 t + \frac{1}{2} (\Gamma_1 t)^2 \right) - \frac{1}{\Gamma_2} \left(1 - \Gamma_2 t + \frac{1}{2} (\Gamma_2 t)^2 \right) \right]$$

$$P_{1+1} \approx \frac{1}{2} \Gamma_1 \Gamma_2 t^2 = \frac{1}{2} \sigma_1 \sigma_2 \left(\frac{I}{\hbar \omega} \right)^2 t^2 \quad (\text{S2})$$

Non-Resonant Multiphoton Ionization

The N -photon non-resonant ionization rate is

$$\Gamma_N = \sigma_N \left(\frac{I}{\hbar \omega} \right)^N$$

where σ_N is the multiphoton ionization cross section giving an ionization probability after a time t

$$P_N(I) = 1 - \exp\left(-\sigma_N \left(\frac{I}{\hbar \omega} \right)^N t\right) \quad (\text{S3})$$

Ion Yield from a Constant Gas Density Target

Focussed Laser Beam

The ionization rate $\Gamma(I)$ is a function of the intensity and therefore varies in space and time in the interaction region. The spatial dependence of this interaction becomes very strong when the beam is focussed. For a beam with a gaussian spatial profile, temporal profile $f(t)$ and peak intensity I_0 focused by a spherical lens or mirror with no diffraction effects, the intensity is given by

$$I(r, z, t) = \frac{I_0}{1 + \left(\frac{z}{z_0}\right)^2} \exp\left(-\frac{2r^2}{w_0^2 \left(1 + \left(\frac{z}{z_0}\right)^2\right)}\right) f(t) \quad (\text{S4})$$

where w_0 is the waist radius defined as the distance from the axis at which the intensity drops to $1/e^2$,

$z_0 = \frac{\pi w_0^2}{\lambda}$ is the Rayleigh length defined as the distance along the propagation direction at which the intensity reduces by a factor of 2.

The probability of ionization in at a position r, z is given by

$$P(r, z) = 1 - \exp\left(-\int_{-\infty}^{+\infty} \Gamma(I(r, z, t')) dt'\right)$$

which for a rectangular pulse profile of length τ is simply $P(r, z) = 1 - \exp(-\Gamma(I(r, z))\tau)$.

The ion yield is obtained by integrating over the whole interaction volume. Assuming the gas has a constant number density n , for a volume of space $r \rightarrow r + dr, z \rightarrow z + dz$, the number of ions produced is

$$dY = n P(I(r, z)) dV$$

To find the total yield, it is more convenient to do this integration over shells of equal intensity

$$Y = n \int_0^{V^{max}} P(V) dV = n \int_{I_0}^{I^{min}} P(I) \frac{dV}{dI} dI \quad (S5)$$

$\frac{dV}{dI}$ represents the intensity shell over which the integration is performed from the maximum intensity I_0

(which corresponds to an interaction volume of zero) to some minimum intensity below which the ion yield

can be neglected. $\frac{dV}{dI}$ can be determined by obtaining an expression for the volume which encloses all

intensities greater than I . Integrating along z to get the volume inside the iso-intensity boundary defined by I gives

$$V = \int_{-z_{max}}^{+z_{max}} \pi r^2 dz$$

Rearranging Eqn S4 to obtain an expression for r^2

$$V = \int_{-z_{max}}^{+z_{max}} -\frac{\pi w_0^2}{2} \left(1 + \left(\frac{z}{z_0}\right)^2\right) \ln\left(\frac{I}{I_0} \left(1 + \left(\frac{z}{z_0}\right)^2\right)\right) dz$$

$$z_{max} = z_0 \xi$$

$$\text{where } \xi = \left(\frac{I_0}{I} - 1\right)^{1/2}$$

Making the substitution $x = \frac{z}{z_0}$

$$V = -\pi w_0^2 z_0 \int_0^\xi (1 + x^2) \ln\left(\frac{1+x^2}{1+\xi^2}\right) dx$$

Integration yields ¹

$$V = -\frac{\pi^2 w_0^4}{\lambda} \left[x \ln\left(\frac{1+x^2}{1+\xi^2}\right) + \frac{1}{3} x^3 \ln\left(\frac{1+x^2}{1+\xi^2}\right) - \frac{2}{9} x^3 - \frac{4}{3} x + \frac{4}{3} \tan^{-1} x \right]_0^\xi$$

$$V = V_0 \left(\frac{2}{9} \xi^3 + \frac{4}{3} \xi - \frac{4}{3} \tan^{-1} \xi \right) \quad (S6)$$

$$\text{where } V_0 = \frac{\pi^2 w_0^4}{\lambda}$$

When $I_0 \gg I$, only the first term is significant giving

$$V(I_0 \gg I) \rightarrow \frac{2}{9} V_0 \xi^3 = \frac{2}{9} V_0 \left(\frac{I_0}{I}\right)^{3/2}$$

Therefore the volume within an iso-intensity surface increases as $I_0^{3/2}$ which is why the ion yield increases with this trend when the peak intensity significantly exceeds the intensity at which ionization saturates.

Returning to the general case, differentiating eqn. S6 gives

¹ <http://integrals.wolfram.com/>

$$\frac{dV}{dI} = -\frac{1}{3} \frac{V_0}{I_0} \xi (1 + \xi^2) (3 + \xi^2)$$

$$\frac{dV}{dI} = -\frac{1}{3} \frac{V_0}{I} \left(\frac{I_0}{I} - 1 \right)^{1/2} \left(\frac{I_0}{I} + 2 \right) \quad (\text{S7})$$

The fact that $\frac{dV}{dI} < 0$ simply indicates that the volume of the shell decreases as the intensity at the boundary increases (while I_0 is constant). From eqn. S5 the total ion yield is

$$Y = \frac{nV_0}{3} \int_{I_{min}}^{I_0} \frac{P(I)}{I} \left(\frac{I_0}{I} - 1 \right)^{1/2} \left(\frac{I_0}{I} + 2 \right) dI \quad (\text{S8})$$

Unfocussed Laser Beam

Consider interaction of a minimally diverging laser beam with gaussian spatial profile and a full width half maximum of D . The intensity at a radius r is

$$I(r) = I_0 \exp\left(-4 \ln 2 \left(\frac{r}{D}\right)^2\right)$$

Ions are collected from a length L of the interaction between the laser and gas. The volume of the beam experiencing an intensity I is $dV = 2\pi r L dr$. If the intensity and ionization probability is low ($P \ll 1$), the ionization probability for a N -photon non-resonant process is

$$P = \sigma_N \left(\frac{I}{\hbar\omega} \right)^N \tau$$

Therefore the number of ions produced due to interactions at intensity I with a gas of density n is

$$dY_N = P n dV = 2\pi L \sigma_N \left(\frac{I}{\hbar\omega} \right)^N \tau n r dr$$

Integrating this to obtain the total ion yield Y gives

$$Y_N = \frac{\pi L n}{4N \ln 2 (\hbar\omega)^N} D^2 \tau \sigma_N I_0^N$$

For $N = 3$, in terms of the laser pulse energy E , this becomes (where for a gaussian beam $I_0 = \frac{4 \ln 2}{\pi} \frac{E}{\tau D^2}$)

$$Y_3 = \frac{16(\ln 2)^2 L n \sigma_3}{3\pi^2 (\hbar\omega)^3 D^4} \frac{E^3}{\tau^2} \quad (\text{S9})$$

For the resonant two photon ionization case using the ionization probability from equation S2 gives

$$Y_{1+1} = \frac{(\ln 2) L n \sigma_1 \sigma_2}{(\hbar\omega)^2 \pi D^2} E^2 \quad (\text{S10})$$