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Conceptual Basis of Resonance Ionization Spectroscopy

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1. Introduction

Resonance Ionization Spectroscopy (RIS) can be defined as a state-selective detection process in which tunable lasers are used to promote transitions from the selected state of the atoms or molecules in question to higher states, one of which will be ionized by the absorption of another photon. At least one resonance step is used in the stepwise ionization process, and it has been shown (Hurst et al 1975, 1978, 1979, 1980; Payne et al 1981a; Chen et al 1984) that the ionization probabili y of the spectroscopically selected species can nearly always be made close to unity. Since measurements of the number of photoelectrons or ions can be made very precisely and even one electron (or under vacuum conditions, one ion) can be detected, the technique can be used to make quantitative measurements of very small populations of the state-selected species. Counting of individual atoms has special meaning for detection of rare events.

The ability to make saturated RIS measurements opens up a wide variety of applications to both basic and applied research. In reviews of RIS (Hurst et al 1975, 1978, 1979, 1980; Payne et al 1981a) the subject was treated generally, including the underlying photophysics applications, the ability to use it to count single atoms, and its applications to measurements in atomic and molecular physics. We view RIS as a specific type of multi-photon ionization in which the goal is to make quantitative measurements of quantum-selected populations in atomic or molecular systems. This goal is attained by requiring that the selective excitation steps be resonant in nature and involve only one- or two-photon (only one-photon if at all possible) absorption processes, thereby allowing the entire process to be carried to saturation without loss of spectroscopic selectivity due to laser power induced shifts or broadening.

2. Two-State Model of Laser Excitation

Work with narrow bandwidth dye lasers is nearly always carried out under circumstances where the number of photons per mode of the electromagnetic field is very large. This limiting case is one in which the electromagnetic field is near the correspondence principle limit and can be described with either semiclassical or classical formalism. The approach described here takes advantage of this limiting case so that the atoms interacting with the laser field are treated quantum mechanically, but the laser field is treated classically. This approach was used extensively

in spin resonance work long before the discovery of lasers, and has been used by Lamb (1964) and others in developing an understanding of gas lasers. Within this limit, Power and Zineau (1959) have shown that the interaction between an atom or molecule and a laser field can be taken to be

$$V = -\vec{P}_{op} \cdot \vec{E}(t) ,$$

where $\vec{P}_{op}$ is the electronic dipole operator of the atom or molecule and $\vec{E}(t)$ is a classical electromagnetic wave representing the electric field due to the laser. It has been shown that this form of the interaction accounts properly for laser field-induced shifts and widths and other effects that occur when intense laser light is tuned near dipole allowed one- or two-photon resonances. Thus, Eq. (1) can be used even when it is necessary to include V to all orders.

There are limits to the validity of Eq. (1) which occur when the laser is tuned near higher multipole resonances, or when the effects of spontaneous emission are important. Spontaneous emission can be included phenomenologically by introducing into the equations of motion an appropriate damping term and by interpreting the eigenenergies in the atom as being "dressed" by the vacuum electromagnetic field. The Wigner-Weisskopf approximation provides a formal way of starting with a quantized treatment and introducing spontaneous emission and Lamb shifts; yet one can still get back to the results of our classical treatment by replacing certain occupation numbers of the modes of the laser field in such a way that $n_{\vec{k}}$ and $n_{\vec{k}} \pm 1$ are interpreted as having the same value and a classical electric field amplitude is introduced as proportional to $\sqrt{n_{\vec{k}}}$. (In cgs units, I = power density = $N\hbar\omega c = E_0^2 c/8\pi$ where $N\hbar\omega$ is the energy density of the occupied modes of the laser field.)

We will now discuss in an elementary way the problem of atomic response when a laser is tuned near a strong dipole allowed, one-photon resonance. We treat the laser field classically and assume that a classical path treatment of atomic motion is appropriate. Thus, we assume that the position of the nucleus of the atoms is $\vec{r}(t) = \vec{r}_0 + \vec{v}t$, where $\vec{r}_0$ is the position vector at t = 0 and $\vec{v}$ is the velocity of the atom. The laser field at the position of the atom becomes

$$\vec{E} = \vec{E}_0 \cos[\omega t - \vec{k} \cdot \vec{r}(t)]$$

$$= \vec{E}_0 \cos(\omega t - \vec{k} \cdot \vec{v} t - \theta_0) .$$

We write the Hamiltonian for the electrons as

$$H = H_0 - \vec{P}_{op} \cdot \vec{E} - i \frac{\gamma\hbar}{2} |1\rangle\langle 1| ,$$

where H_0 is the Hamiltonian of the isolated atom, $-\vec{P}_{op} \cdot \vec{E}$ is the atom field interaction, and the nonhermetian term is a decay term for the excited state $|1\rangle$ associated with spontaneous emission. We label the eigenstates of H_0 as $|i\rangle$, where $H_0|i\rangle = \hbar\omega_i|i\rangle$, and $\langle i|j\rangle = \delta_{ij}$ for discrete states. If we expand the state vector $i\hbar\partial|\psi(t)\rangle/\partial t = H|\psi(t)\rangle$ and use the orthogonality of the state vectors $|i\rangle$, we obtain

$$i\hbar \frac{da_m}{dt} = -\sum_n a_n e^{i(\omega_m - \omega_n)t} \langle m|\vec{P}_{op} \cdot \vec{E}|n\rangle - i\hbar \frac{\gamma}{2} a_m \delta_{m,1}$$

where a_m are amplitudes for $|m\rangle$ in the interaction representation. We

assume that initially $|\psi(0)\rangle = |0\rangle$, where $|0\rangle$ is the ground state. Initially, only a_0 is nonzero. If ω is very close to $\omega_1-\omega_0$ and we consider $m = 1$, we see that there is only one term on the right hand side that does not oscillate very rapidly so that the individual contributions to the sum average to a value near zero. The non-vanishing term is that with $n = 0$. It has the form

$$e^{i(\omega_1-\omega_0)t}\, E_0 \cos[\omega(t - \vec{k}\cdot\vec{v}_0] = \frac{E_0}{2}\, e^{i(\omega_1-\omega_0-\omega\, +\, \vec{k}\cdot\vec{v})t}\, e^{-i\theta_0} + \frac{E_0}{2}\, e^{i(\omega_1-\omega_0+\omega\, -\, \vec{k}\cdot\vec{v})t}\, e^{i\theta_0} .$$

One of the complex exponential terms oscillates very rapidly, but when $\omega_1-\omega_0-\omega$ is small, the other oscillates very slowly by comparison. It is the one slowly oscillating term which accounts for most of the net rate of change in a_1. Thus,

$$i\hbar \frac{da_1}{dt} = -\frac{\langle 1|\vec{P}_{op}\cdot\vec{E}_0|0\rangle}{2}\, a_0\, e^{i(\omega_1-\omega_0-\omega\, +\, \vec{k}\ \ \vec{v})t}\, e^{-i\theta_0} - i\hbar\frac{\gamma}{2}\, a_1 .$$

Correspondingly, when $m = 0$ there is only one slowly oscillating term on the right hand side of Eq. (4) that accounts for nearly all of the net change in a_0 and we find

$$i\hbar \frac{da_0}{dt} = -\frac{\langle 0|\vec{P}_{op}\cdot\vec{E}_0|1\rangle}{2}\, a_1\, e^{-i(\omega_1-\omega_0-\omega\, +\, \vec{k}\ \ \vec{v})t}\, e^{i\theta_0} .$$

Let $\delta = \omega-\omega_1+\omega_0 - \vec{k}\cdot\vec{v}$ be the detuning from resonance, and let $\Omega_R = \exp(-i\theta_0)\ \langle 1|\vec{P}_{op}\cdot\vec{E}_0|0\rangle/\hbar$ be the Rabi frequency. Equations (5) and (6) then become

$$\frac{da_1}{dt} = i\,\frac{\Omega_R}{2}\, e^{-i\delta t}\, a_0 - \frac{\gamma}{2}\, a_1 ,$$

$$\frac{da_0}{dt} = i\,\frac{\Omega_R^*}{2}\, a_1\, e^{i\delta t} .$$

The above set of coupled equations represents a two-state description of atomic response which is appropriate when only a single state is initially populated and a laser is tuned very near resonance between the initial state and a second well isolated state of the atom or molecule.

In general, the Rabi frequency (Ω_R) will also have a time dependence associated either with a pulsed feature of the laser or with the time of passage of the atom across the laser beam. However, it is instructive to study the solution to Eq. (7) when $\Omega_R = 0$ for $t < 0$ and Ω_R = constant for $t \geq 0$. We find

$$|a_1|^2 \simeq \frac{|\Omega_R|^2\, e^{-\frac{\gamma}{2}t}}{\delta^2 + |\Omega_R|^2}\left(\frac{1 - \cos\sqrt{\delta^2 + |\Omega_R|^2}\ t}{2}\right),$$

for either δ or $|\Omega_R| \gg \gamma$. We see that initially $|a_1|^2 \simeq 0$; but if $\delta = 0$, we find at $t = \pi/|\Omega_R|$ that $|a_1|^2 \simeq 1$. There is an oscillatory behavior to $|a_1|^2$ in which it varies between zero and unity with a laser power-dependent frequency. When $|\Omega_R| \gg \gamma$, we see that as long as $|\delta| \ll |\Omega_R|$, $|a_1|^2$ may become close to unity even though the laser is not tuned to resonance. When $|\delta| = |\Omega_R|$, the value of $|a_1|^2$ can rise to 0.5, so that

the linewidth is power dependent with a full width at half maximum of $2|\Omega_R|$. If a second laser is present which is not resonant with any discrete-discrete transitions involving states $|0\rangle$ and $|1\rangle$, and which ionizes the upper state at a rate which is small compared with $|\Omega_R|$ but large compared with γ, a linewidth for the ionization signal will be $2|\Omega_R|$ as well.

The one-photon Rabi frequency can be written as $|\Omega_R| = P_{10}E_0/\hbar$, where $P_{10} = \langle 1|\vec{P}_{op}\ \vec{E}|0\rangle$, with $\vec{E}$ being the polarization unit vector. The power density of the laser is $I = cE_0^2/8\pi$ in ergs/sec-cm^2 and P_{10} can be expressed as $ea_B\rho$ where e is the electron charge and a_B is the Bohr radius. The ρ in P_{10} is dimensionless and represents the matrix element of $\vec{P}_{op}\ \vec{e}$ in atomic units. For a strong transition, ρ is of the order of unity. Expressing E_0 in terms of power density in W/cm^2, we find

$$|\Omega_R| \simeq 2 \times 10^8 \rho\ [I(W/cm^2)]^{1/2},$$

where $|\Omega_R|$ is in units of radian/sec. We see that for a strong transition for $I = 1$ W/cm^2, $|\Omega_R| \simeq 2 \times 10^8$/sec, which is already comparable to or larger than γ, the spontaneous decay rate. For a J=0 to J=1 transition, $\rho = [13.6\ eV/\hbar\omega_T\ (eV)]\ F_{01}$, where F_{01} is the absorption oscillator strength of the transition and $\hbar\omega_T$ is the excitation energy in eV.

Consider an example in which narrow bandwidth light at 116.48 nm is used to pump the transition $4p^6$ (J=0) $\rightarrow$ $4p^5 6s'$ (J=1) in krypton. In the latter case, $F_{01} = 0.173$. We find

$$|\Omega_R| = 9.4 \times 10^7\ \ [I(W/cm^2)]^{1/2}\ .$$

With a peak power of 1 W in a 1-mm beam diameter, we find $|\Omega_R| \simeq 1.06 \times 10^9$/sec. With a pulse length of 3×10^{-9} sec, the population would very nearly be inverted in the absence of Doppler effects when such a pulse is tuned to the 116.48-nm resonance. The Doppler width is about 2×10^{10}/sec so that only atoms with Droppler shifts less than 10^9/sec are excited efficiently. In the situation described above, a little less than 10% of the krypton atoms in the 1-mm beam are excited. However, if additional resonance states are used with transition energies less than 2 eV, the Doppler width for further excitation is $<2 \times 10^8$/sec which is $\sim 10^{-3}$ cm^{-1}. Thus, after such a transition the pumping of further resonance steps is nearly Doppler free. In our example the required VUV is 3 nJ which should be achievable by frequency tripling light generated by frequency doubling light obtained by injection locking a pulsed amplifier with light from a ring dye laser.

For transitions in the visible, even higher power densities are obtained by operating a jet stream dye laser in a cavity dump mode with pulse repetition rates $>10^6$ Hz. Even transitions from excited states to Rydberg states with $n \cong 13$ have oscillator strengths $>10^{-3}$, so that for such transitions $|\Omega_R| \gtrsim 10^7\sqrt{I(W/cm^2)}$. Such states (i.e., $n \gtrsim 13$) with $\ell \geq 1$ have photoionization cross sections $\gtrsim 10^{-16}$ cm^2 near threshold and can be efficiently ionized by light from a 200-W CO_2 laser (the $n \gtrsim 13$ states have ionization potential less than 0.1 eV). With 10^{-8}-sec pulses from the cavity dumped dye laser, about 20-W peak power is required for efficient excitation to the Rydberg state with a 1-mm diameter beam. With a proper design of a continuous thermal atomizer, it may be possible to ionize several percent of a selected isotope as it is evaporated by using a combination of two or more jet stream or ring dye lasers operating in a

cavity dump made along with a cw CO_2 laser. Perhaps 40% of the elements can be ionized with such a scheme. Such a RIS scheme may impact resonance ionization mass spectrometry (RIMS) in a significant way.

In the above discusson of excitation with Fourier transform limited bandwidth lasers, the changes in a_0 and a_1 in different time intervals add with constructive interference and a rate equation discussion is not appropriate. However, when the laser bandwidth is much greater than $|\Omega_R|$, the time can be course grained into intervals large compared with the coherence time but short compared with $1/|\Omega_R|$. The changes in a_0 and a_1 from different time intervals are then randomly phased and rate equations are appropriate. One can then show that in the absence of collisions and with the bandwidth also greater than the Doppler width that for $J = 0 \rightarrow J = 1$ transitions,

$$\sigma_a = \sigma_s = \frac{2\pi^{3/2}}{\sigma}\left(\frac{e^2}{m_e c}\right) F_{01}\, e^{-(\delta^2/2\sigma^2)} ,$$

where the laser lineshape is assumed to be $\exp[-(\omega-\bar{\omega})^2/2\sigma^2]$, $\delta = \bar{\omega}-\omega_r$, σ_a = absorption cross section, σ_s = stimulated emission cross section, and the light is plane polarized. We find

$$\sigma_a(\mathrm{cm}^2) = 8.32 \times 10^{-13} \left[F_{01}/\mathrm{FWHM}(\mathrm{cm}^{-1})\right] .$$

Since in argon, krypton, and xenon many transitions to the lowest s states have $F_{01} \simeq 0.2$, we see that for VUV light with FWHM = 0.2 cm^{-1} that the absorption cross section is close to 10^{-12} cm^2. It is somewhat easier to generate VUV light with a bandwidth of ~1 cm^{-1}, in which case $\sigma_a(\mathrm{cm}^2) = 10^{-12} F_{01}$.

It has recently been shown (Tomkins and Mahon 1981) that if one uses a cell with mercury vapor at a concentration of $\sim 10^{17}/\mathrm{cm}^3$, a four-wave mixing scheme can be used to generate $\sim 10^{13}$ photons at 125.02 nm in a beam of diameter ~1 mm. Thus, the photon fluence is $\sim 10^{15}/\mathrm{cm}^2$ and the pulse length is ~5 ns. The product of the absorption cross section and the photon fluence for the $5p^6 \rightarrow 5p^5 5d[1/2]_1$ transition in xenon is $\sim 1000\, F_{01}$. The oscillator strength of this transition is believed to be $F_{01} = 0.01$, so that the transition is strongly saturated. Consequently, it is relatively easy to carry out saturated ionization of xenon even with a 3-mm beam diameter.

We were not so lucky as to have a ready-made VUV source available in the cases of argon and krypton. However, other work (Hilbig and Wallenstein 1981, Kramer et al 1983) has demonstrated that mixtures of xenon and argon serve as an effective media for four-wave mixing in many wavelength regions between 104 nm and 147 nm. The oscillator strengths of the lowest $p \rightarrow s$ transitions in argon and krypton are much larger than 0.06, and effective ionization over a 1-mm beam is adequate so that $>10^{11}$ photons per pulse with a pulse length ~3 ns and a bandwidth 1 cm^{-1} is a reasonable goal. If the 10^{11} photons/pulse can be generated at one-photon resonance, we will be close to saturation over a 1-mm diameter and the fundamental or second harmonic of a dye laser can be used to saturate a second transition to a high-lying state that can either be ionized by the fundamental of a Nd:YAG laser or a CO_2 laser. With such a scheme, ionization probabilities near unity can be obtained over most of a 1-mm diameter beam. It would be advantageous to separate the generated VUV from the laser beams used to generate it, so that the only short wavelength light entering an

experimental cell has very low intensity. Typically, 10^{13} photons/cm^2 VUV photons will ionize a fraction $\sim 10^{-5}$ of the background molecules having ionization potentials less than the VUV photon energy.

We now consider the possibility of starting with two-photon excitation. With resonant two-photon excitation, equations like Eq. (7) are obtained except the Rabi frequency involved is a two-photon term and a power-dependent a.c. shift enters the equations of motion (Hurst et al 1979, Payne et al 1981a). In this method one can use either very narrow bandwidth lasers and counterpropagating beams, so that the dominant excitation process involves the absorption of one photon from each direction of propagation, or a laser with a bandwidth larger than the Doppler width of the transition. In the case of narrow-bandwidth lasers and counterpropagating beams, an atom with a component of velocity v parallel to the incident beam sees a frequency $\omega(1 + v/c)$ from one beam and a frequency $\omega(1 - v/c)$ from the other. If one photon is absorbed from each direction of propagation, the absorbed energy is $2\hbar\omega$, which is independent of v. On the other hand, if two photons are absorbed from the beam propagating toward the direction of motion, the absorbed energy is $2\hbar\omega(1 + v/c)$. Thus, if $2\hbar\omega$ is exactly resonant with the two-photon transiton, the absorbed frquency is off resonance by $2v\omega/c$. With absortion of one photon from each of the counterpropagating beams, exact resonance is otained independent of v. This "Doppler-free" method of excitation (Vasilenko et al 1970) is even more effective if the counterpropagating beams have slightly different frequencies so that $\hbar(\omega_1+\omega_2)$ equals the difference between the energy of the excited and ground states. In the latter situation an insignificant residual Doppler effect $(\omega_2-\omega_1)v/c$ remains; but when both absorbed photons come from the same beam, the detuning from two-photon resonance can be huge compared with the Doppler width and yet $(\omega_2-\omega_1)v/c$ can still be small compared with the laser bandwidth. As an example of how much power is required to saturate a two-photon transition when Doppler-free excitation is used, consider the transition from $5p^6$ to $5p^56p[1/2](J=0)$ in xenon. We have measured (Chen et al 1980) a two-photon Rabi frequency for this transition, which is in good agreement with calculations (Payne et al 1981b, Pindzola et al 1981), to be $\sim 10\ I(W/cm^2)$ where the two-photon Rabi frequency is in radians/sec and the power density I is in W/cm^2. We see that with a power density of 40 MW/cm^2 the transition is saturated. Consequently, about 0.4 mJ generated at 249.6 nm in a 4-ns pulse and brought to a 0.5-mm beam waist is sufficient to achieve some degree of saturation if the light has a near-transform-limited bandwidth. When only an incident beam is used, it is necessary to use either much higher power densities or a broadband laser in order to ionize all atoms in the 0.5-mm beam. If a laser with a long cavity and a bandwidth of 0.2 cm^{-1} is used to cover the Doppler width, the output at 249.6 nm must be >5 mJ for a 4-ns pulse if saturation is to be achieved over a 1.5-mm beam.

With most commercial dye lasers, it is troublesome to achieve transform-limited bandwidths and the degree of frequency stability required while also having an output of 0.4 mJ/pulse. Perhaps the easiest way to have these characteristics is to start with a cw ring dye laser and use it to injection lock a pulsed amplifier. Nonlinear processes can then be used to achieve output at 249.6 nm. If necessary, the 249.6-nm beam can be amplified in a KrF amplifier. Bakor et al (1980) have demonstrated the practicality of such a scheme, but such a laser system is expensive. The two-photon process with broad bandwidth light (i.e., ~ 0.2 cm^{-1}) requires

>5 mJ of output, which is difficult at 249.6 nm. With power densities >300 MW/cm^2 at 249.6 nm, there is also danger of multiphoton ionization of heavy molecules which could lead to mass interference in the mass spectrometer.

Our considerations of the strongest two-photon transition in xenon lead us to the conclusion that it may be possible to do effective detection of xenon with a relatively inexpensive commercial system which has undergone considerable alteration. In the case of krypton, the strongest two-photon transition has a two-photon Rabi frequency which is more than twice as small and at a much less accessible wavelength than that of the xenon transition. The strongest transition in krypton is $4p^6 \rightarrow 4p^5 5p[1/2]_0$. We believe that krypton would be very difficult to ionize efficiently when the process is started by two-photon absorption. We make this statement despite the fact that Rhodes' group has generated very intense, narrow-bandwidth light near 192.8 nm, which is at two-photon resonance with $4p^6 \rightarrow 4p^5 6p[1/2]_0$. The two-photon Rabi frequency of this transition, at a given power density, is nearly an order of magnitude smaller than that for $4p^6 \rightarrow 4p^5 5p[1/2]_0$. Thus, power densities of >200 MW/cm^2 at 192.8 nm are required and such high intensity, short-wavelength radiation stands a good chance of creating isotopic interferences due to ionization of hydrocarbons and freon. Similar arguments can be made concerning the RIS of argon starting with two-photon excitation.

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