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LECTURE 1

THEORY OF RESONANCE IONIZATION SPECTROSCOPY*

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M. G. Payne and G. S. Hurst

Chemical Physics Section, Health and Safety Research Division

Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830 U.S.A.

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THEORY OF RESONANCE IONIZATION SPECTROSCOPY*

M. G. Payne and G. S. Hurst

Chemical Physics Section, Health and Safety Research Division

Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830 U.S.A.

1. Introduction

Resonance Ionization Spectroscopy (RIS) can be defined as a state selective detection process in which pulsed 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 shown¹ that the ionization probability 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^{1,2} 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

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resonance ionization spectroscopy as a specific type of multiphoton 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. The Fundamental RIS Scheme

It now appears that all atoms except helium and neon can be efficiently ionized by using a scheme in which a sequence of single-photon absorptions promote a valence electron to a high-lying excited state with $\ell \geq 1$, from which ionization occurs due to a relatively intense beam of Nd-YAG radiation at 1.06μ or CO_2 radiation at $\sim 10 \mu$. We will now discuss the laser requirements for a simplified version of an RIS scheme involving only one-photon absorption.

It is well known^{1,2,3} that when Ω_R (the Rabi frequency) and Δ_S (the a.c. Stark shift) for a resonant transition are small compared with the laser bandwidth, a rate equation analysis can be used in describing the interaction of an atom with the laser fields. In particular, in the absence of collisions, which redistribute atomic populations among the magnetic substates within the laser pulse length, we find for co-propagating, plane polarized beams that the cross sections for absorption and stimulated emission are equal and are given by

$$\begin{aligned} \sigma_a &= \sigma_s \\ &= \frac{2\pi^2}{\sqrt{2\pi}\sigma^2} \left(\frac{e^2}{mc} \right) F_{01} e^{-\frac{\Delta^2}{2\sigma^2}} \end{aligned} \quad (1)$$

where $\delta = \bar{\omega} - \omega_r$ is the detuning of the line center of the laser from the resonant angular frequency for the transition, ω_r ; F_{01} is the absorption oscillator strength of the transition; $2\sqrt{2\ln 2} \sigma$ is the full width at half maximum (FWHM) of the laser line shape in angular frequency units; and the laser spectrum is taken to be $(2\pi\sigma^2)^{-1/2} \exp[-(\omega - \bar{\omega})^2/2\sigma^2]$. Thus,

$$\sigma_a (\text{cm}^2) = 8.32 \times 10^{-13} \left(F_{01} / \text{FWHM}(\text{cm}^{-1}) \right), \quad (2)$$

where $\text{FWHM} (\text{cm}^{-1})$ is the laser bandwidth in cm^{-1} . Thus, for a transition with $F_{01} = 0.25$ and a laser bandwidth $\text{FWHM} (\text{cm}^{-1}) \approx 0.2 \text{ cm}^{-1}$, we find $\sigma_a \approx 1 \times 10^{-12} \text{ cm}^2$.

For most atoms it is most difficult to use one-photon absorption for transitions from the ground state to one of the lower lying electronically excited states. In particular, the rare gases, most of the halogens, hydrogen, oxygen, and carbon all require vacuum ultraviolet (VUV) radiation for this initial step. Once the initial excitation is made, other transitions can be pumped by a relatively weak dye laser, usually without even resorting to frequency doubling or mixing. For this reason we focus our attention on the situation in Fig. 1. In Fig. 1 a very weak laser field is used to pump the transition $|0\rangle$ to $|1\rangle$. The population of $|1\rangle$ can be promoted to a higher excited state and ionized on a time scale that is very short compared with the laser pulse length by using only dye lasers with $\text{FWHM} (\text{cm}^{-1}) \approx 0.2 \text{ cm}^{-1}$, power density $= I < 2 \text{ kw/cm}^2$ and pulse length $\leq 5 \times 10^{-9} \text{ sec}$. The Nd-YAG light used for ionization may have $I \approx 5 \times 10^7 \text{ w/cm}^2$ (i.e., 50-mJ pulses of beam area 0.08 cm^2 and pulse length $\sim 10^{-8} \text{ sec}$). The ionizing light will be close to ionization threshold, and in ionizing p, d, or f states the ionization cross section will nearly always

exceed 10^{-17} cm^2 . The ionization of excited s states should be avoided in all but a few light elements due to Cooper minima relatively near threshold and their general characteristic of having ionization cross sections that are two or three orders of magnitude smaller than those of p, d, or f states in the region near threshold.

Since it is easy to deplete $|1\rangle$ by ionization on a time scale that is very fast, the repopulation of $|1\rangle$ due to stimulated or spontaneous emission is negligible when the $|0\rangle \rightarrow |1\rangle$ transition is pumped at a much slower rate. Thus, if $\rho_{00}(\rho, t)$ is the probability that an atom located at a distance ρ from beam axis is in the ground state at time t and $F(\rho, t)$ is the photon flux at ρ at time t :

$$\frac{d\rho_{00}(\rho, t)}{dt} = -\sigma_a F(\rho, t) \rho_{00}(\rho, t). \quad (3)$$

Thus, $P_I(\rho)$, the probability of an atom at ρ being ionized, is given by ($|1\rangle$ is depleted very rapidly)

$$\begin{aligned} P_I(\rho) &= 1 - \rho_{00}(\rho, \infty), \\ &= 1 - \exp\left(-\sigma_a \int_0^\infty F(\rho, t) dt\right), \\ &= 1 - \exp(-\sigma_a \phi(\rho)), \end{aligned} \quad (4)$$

where $\phi(\rho)$ is the number of photons/cm² at ρ . In order for Eqs. (3) and (4) to hold for all ρ values where $P_I(\rho)$ is significant, the dye and Nd-YAG lasers used to ionize $|1\rangle$ have beam radii about three times larger than that used for the $|0\rangle$ to $|1\rangle$ transition.

If N is the concentration of the selected population and $\phi(\rho) = \phi(0)\exp(-2\rho^2/d^2)$,

$$\begin{aligned}
N_I &= \text{number of ions produced in length } L \text{ of the laser beams} \\
&= NL \int_0^\infty 2\pi\rho \, P_x(\rho) d\rho, \\
&= \frac{N\pi d^2 L}{2} \int_0^\infty x dx [1 - \exp(-\sigma_a \phi(0) e^{-x^2})], \\
&= \frac{\pi N L d^2}{2} T(\sigma_a \phi(0)).
\end{aligned} \tag{5}$$

The function $T(x)$ has the power series

$$T(x) = \sum_{n=1}^{\infty} \frac{(-1)^{n+1} x^n}{n(n!)} . \tag{6}$$

The number of photons is related to d and $\phi(0)$ by $N_p = \pi\phi(0)d^2/2$. Thus, if $d = 0.1$ cm, $N_p = 2 \times 10^{10}$ photons/pulse, $F_{01} = 0.19$, and $\text{FWHM} (\text{cm}^{-1}) = 0.2 \text{ cm}^{-1}$, we find $\sigma_a \phi(0) \approx 1$ and $N_I = NL\pi(d^2/2)(0.39) = NL^*(6.1 \times 10^{-3} \text{ cm}^2)$.

3. Four-Wave Mixing in Xenon and Mercury

Important advances in VUV generation have been made by several workers.⁴ Cotter⁵ and Wallenstein et al.⁶ have shown that third-harmonic generation in argon, krypton, and xenon can yield 1-10 w peak power for much of the region $1100 \text{ \AA} \leq \lambda \leq 1470 \text{ \AA}$. Four-wave mixing with a two-photon resonant enhancement has been used by Wallenstein et al.⁶ and Tomkins and Mahon⁷ in order to generate several $\mu\text{J}/\text{pulse}$ in mercury. In particular, the latter workers have generated several μJ at $1250.2 \text{ \AA}$, and this provides a very effective source to begin the RIS of xenon.

Very crudely, the presence of intense laser light in a gaseous medium causes the atomic wave function to evolve from $|\psi(-\infty)\rangle = |0\rangle$ to $|\psi(t)\rangle = \sum_n a_n(t) \exp[-i\omega_n t] |n\rangle$.

In particular, if light is present which is two-photon resonant with a higher state, then $a_0(t)$ is reduced but the amplitude for the higher state increases. When intense light is also present which is close to resonance between the two-photon resonance and a higher excited state $|L_3\rangle$ having allowed transitions back to the ground state, $|\psi(t)\rangle$ has three significant amplitudes (i.e., the ground state, the two-photon resonance state, and the near three-photon resonance). Thus, if we consider the expectation value of the electronic dipole operator, $\vec{P}(t) = \langle \psi(t) | \hat{P} | \psi(t) \rangle = \sum_m \sum_n a_n^*(t) a_m(t) \exp[i(\omega_n - \omega_m)t] P_{nm}$. The amplitude of $|L_3\rangle$ is enhanced both because of the two-photon resonance and the near three-photon resonance induced by the second laser. Since $|\langle 0 | \hat{P} | L_3 \rangle| \neq 0$, the individual atoms develop strong dipoles oscillating at $2\omega_1 + \omega_2$, where ω_1 is the angular frequency of the laser which is tuned near two-photon resonance.

In order to achieve a strong signal at $2\omega_1 + \omega_2$, the pressure (and perhaps a buffer gas partial pressure as well) must be adjusted so that a large degree of constructive interference occurs at the desired wavelength. When the laser beams are unfocused, strong constructive interference occurs when $\Delta k = 2k(\omega_1) + k(\omega_2) - k(2\omega_1 + \omega_2) = 0$, where $k(\omega)$ is the length of the wave vector for light at frequency ω . This is just the condition for the phase of a driven oscillator to be such that it generates a radiation field which is in phase with the combined field due to other atoms upstream in the laser beam.

Table 1 shows levels in xenon and mercury where two- and near three-photon resonances could be combined in order to generate sizeable

quantities of photons at $2\omega_1 \pm \omega_2$ (~ when $|L_3\rangle$ lies lower than the two-photon resonance). We have done preliminary studies in which 30 μJ of 2525 Å light was combined with 100 μJ of 1.48 Å light to generate ~1.5 nJ at 1164.8 Å. By increasing the input power we shall reach >100 nJ.

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Figure and Table Captions

Fig. 1. Energy level diagram for a resonance ionization process involving only one-photon stepwise processes.

Table 1. Table of two- and three-photon resonance transitions in Xe and Hg. Each three-photon resonance borders a region of resonant enhancement for the process $2\omega_1 + \omega_2$ or $2\omega_1 - \omega_2$.

FOUR-WAVE MIXING

SYSTEM	$ 0\rangle$	$ 1\rangle$	$ 2\rangle$	λ_1	λ_2	$\lambda_r \rightarrow 2\omega_1 + \omega_2$
Xe	$5p^6$	$5p^5 6p$	$5p^5 7s$	2496Å	1.879 μ	1170.3Å
Xe	$5p^6$	$5p^5 6p$	$5p^5 8s$	2496Å	9247Å	1099.7Å
Xe	$5p^6$	$5p^5 6p$	$5p^5 9s$	2496Å	7506Å	1070.4Å
Xe	$5p^6$	$5p^5 6p$	$5p^5 10s$	2496Å	6818Å	1054.9Å
Xe	$5p^6$	$5p^5 6p$	$5p^5 11s$	2496Å	6463Å	1046.1Å
Xe	$5p^6$	$5p^5 6p'$	$5p^5 5d$	2226Å	10,128Å	1250.2Å
Xe	$5p^6$	$5p^5 6p'$	$5p^5 6s$	2226Å	4584Å	1470Å *
Xe	$5p^6$	$5p^5 6p'$	$5p^5 6s'$	2226Å	7890Å	1296Å *
Xe	$5p^6$	$5p^5 6p$	$5p^5 7d$	2496Å	8327Å	1085Å
Xe	$5p^6$	$5p^5 6p$	$5p^5 7s$	2560Å	1.41 μ	1170.3Å
Hg	$6s^2$	$6s7s$	$6s6p$	3128.5Å	1.014 μ	1849.5Å *
Hg	$6s^2$	$6s7s$	$6s7p$	3128.5Å	1.744 μ	1435.5Å
Hg	$6s^2$	$6s7s$	$6s8p$	3128.5Å	7731Å	1301Å
Hg	$6s^2$	$6s7s$	$6s9p$	3128.5Å	6236Å	1250.6Å
Hg	$6s^2$	$6s7s$	$6s10p$	3128.5Å	5805Å	1232.2Å
Hg	$6s^2$	$6s8s$	$6s6p$	2688.0Å	4917Å	1849.5Å *
Kr	$4p^6$	$4p^5 6p$	$4p^5 5s$	1934.9***	4455Å	1235.8Å *
Kr	$4p^6$	$4p^5 5p'$	$4p^5 5s'$	2023.1**	7887Å	1164.9Å *

* $2\omega_1 - \omega_2 \rightarrow$ WIDE RANGE OF TUNABILITY ON EITHER SIDE OF LINE.

**BY RAMAN SHIFTING 1936Å IN $H_2 \leftrightarrow$ 1936Å BY ArF AMPLIFIER.

***INJECTION LOCKED ArF LASER.

Fig. 1