

Thermal Photoionization in Resonance Ionization Spectroscopy

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Abstract. In Resonance Ionization Spectroscopy, neutral atoms are usually produced by thermal effects, using an oven or a hot surface at high temperature. The radiation from these thermal sources is intense enough to effectively contribute to the photoionization of atoms excited by laser pumping. We show that, for the most common experimental conditions, the ratio of thermal to laser photoionization can be higher than one for excited levels which lie as far as a few thousand cm^{-1} below the ionization threshold. This result is obtained with the use of the analytic expression for the photoionization cross-section of a hydrogen-like atom. We suggest two applications of this thermal photoionization. Namely, the study of highly excited states and Quasi Resonance Ionization Spectrometry, using only one laser of low radiance.

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Difficulties arise in the interpretation of Resonance Ionization Spectroscopy (RIS) spectra, as pointed out in [1], when a thermal atomization source is used [2–8]. In such a case, RIS spectra may show features which depend on laser power, on laser spectral linewidth and on source temperature. Variations of those features make the interpretation of the possible photoionization mechanisms and the identification of the exact photoionization wavelengths difficult, at best. A typical example is the case of Nd, where, of the 43 ionization peaks observed in the 423–463 nm spectral interval, only 23 transitions were identified [5].

We observed similar phenomena in a Resonance Ionization Mass Spectrometry study of Gd in the

430–450 nm spectral range [4]. The atomic vapor was produced, in that study, by a Rh filament heated at ≈ 2000 K. It was thus found that for a laser irradiance of $50 \times 10^{23} \text{ cm}^{-2} \text{ s}^{-1}$, the Gd⁺ spectrum was extremely complex and its details difficult to interpret, while at a laser irradiance of $10^{23} \text{ cm}^{-2} \text{ s}^{-1}$ the spectrum was much simpler. Moreover, in the second case only a few strong lines with an intensity *independent* of laser irradiance were observed. In other words, the second spectrum was saturated and simple while the first was neither.

In the spectral domain investigated, Gd atoms cannot be directly ionized from the ground state by a two-photon absorption process. Nevertheless, we could associate to those saturated strong lines, transitions which originate from the ground state configuration, i.e. the ionization process was a three-photon one. For the non-saturated lines, at high irradiance, we associated a two-photon photoionization process originating from metastable states. It seems strange and it is difficult to understand how a *three-photon* process from the ground state can be more efficient than a *two-photon* one from metastable states.

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This paradox could possibly be explained by taking into account that, when a thermal atomization source is used, the thermal photoionization process can be a very efficient scheme to photoionize an excited atomic state, even if the latter lies far (a few thousand cm^{-1}) below the ionization limit. In this work then, we estimate the relative importance of laser and thermal photoionization from excited states, not close to the ionization threshold.

Theory

The neutral atoms are produced in a relatively high temperature cavity. We assume that a saturated population of excited atoms A_n is produced within the cavity, during the laser pulse, from the atomic ground state A_0 by a two-photon excitation process at the same frequency ν_L . It is well known that, the excitation of an atom with an intermediate state $A_k = (A_n - A_0)/2$, by radiation near the frequency $\nu_L \approx (A_n - A_0)/2h$ is very efficient and that, the population of the final state can be saturated with a relatively low intensity. The relative position of all pertinent levels is depicted in Fig. 1. We will not be further concerned with the details of how the atoms are brought into the saturated excited states by the laser. These excited atoms are then exposed to the thermal radiation in the cavity and,

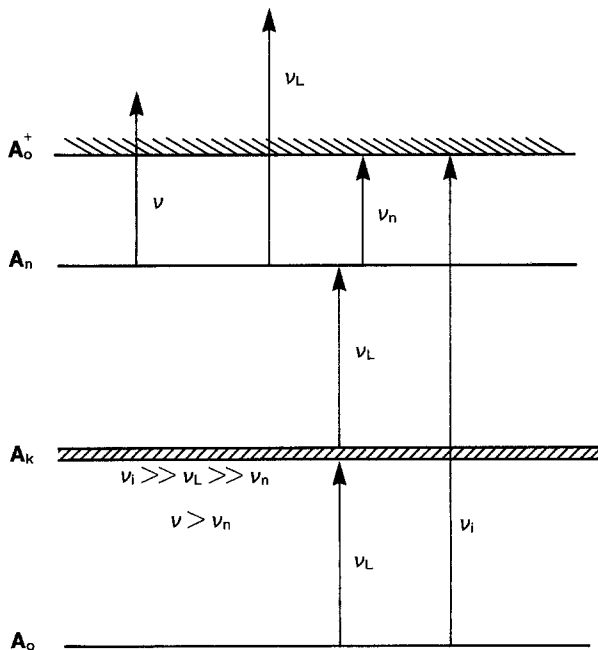
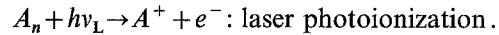
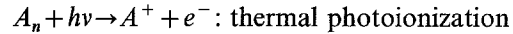


Fig. 1. Schematic of the excitation and ionization processes considered herein, and of the pertinent atomic levels. A_0 is the atom ground state with an ionization frequency ν_i , ν_L is the laser photon frequency, A_k is the intermediate state, A_n is the excited state and its ionization frequency is ν_n , ν is the thermal photon frequency, and A_0^+ is the ion ground state

during the pulse, to the laser itself, and they can be ionized either by thermal or by laser photons:



The relative efficiency of thermal to laser ionization can be determined as the ratio R of the number of ions created by the two processes. The exact calculation of R should take into account that the residence time of the atoms in the thermal field is greater than their residence time in the laser field. This because the duration of the latter is generally quite short (≈ 10 ns), i.e. shorter than the typical lifetime of excited atoms. But our intention is to obtain a rough estimate of the relative efficiency of the two photoionization processes. To that effect, we will approximate R with its value R_m such that the latter is equal to the ratio of the number of ions produced by the two processes during the laser pulse only. Therefore R_m is necessarily a minimum value of R and is equal to the ratio of the two ionization rates:

$$R_m = \frac{\phi(\nu_n)}{F\sigma^+(\nu_L)}. \quad (1)$$

Here $\sigma^+(\nu)$ is the total photoionization cross section, F is the laser photon irradiance, and the thermal ionization rate $\phi(\nu_n)$ is given by [9]:

$$\phi(\nu_n) = \int_{\nu_n}^{\infty} \frac{4\pi I_\nu}{h\nu} \sigma^+(\nu) d\nu. \quad (2)$$

I_ν is the spectral radiance in the cavity and is given by Planck's formula [9]:

$$I_\nu = \frac{2h\nu^3}{c^2} \cdot \frac{1}{e^{h\nu/kT} - 1}. \quad (3)$$

We shall assume that the excited electron is moving in a pure Coulomb potential, since analytic expressions for photoionization cross sections are only available for hydrogen-like atoms. For a dipole electron transition from a bound state (n, l) to a free (continuum) state, the total cross section for absorption of an "unpolarized" photon of frequency ν has been calculated [10–12]. We can write:

$$\sigma^+(\nu) = \frac{8}{3\sqrt{3}\pi^2} \frac{nh^3}{Z^2 m^2 e^2 c} g(\nu, n, l, Z) \left[\frac{\nu_n}{\nu} \right]^3, \quad (4)$$

where $g(\nu, n, l, Z)$ is the Gaunt factor, $h\nu_n$ is the ionization potential of the excited state A_n (see Fig. 1) and $h\nu$ is the energy of the incident photon. If $h\nu$ is less than $h\nu_n$ then $\sigma^+(\nu) = 0$. Moreover, when the incident photon is

in a specific polarization, expression (4) must be divided by two. On substituting Eqs. (2–4) in (1) we obtain:

$$R_m = \frac{16\pi}{Fc^2} \int_{\nu_n}^{\infty} \frac{g(\nu, n, l, Z)}{g(\nu_L, n, l, Z)} \left[\frac{\nu_L}{\nu} \right]^3 \times \frac{\nu^2}{e^{h\nu/kT} - 1} d\nu. \quad (5)$$

Because the Gaunt factor is a slowly-varying function of the frequency [11, 12], especially in the visible and the ultraviolet, we can set the ratio of the two Gaunt factors in (5) equal to unity:

$$R_m = \frac{2\pi c}{F} \left[\frac{2\nu_L}{c} \right]^3 \int_{\nu_n}^{\infty} \frac{1}{\nu(e^{h\nu/kT} - 1)} d\nu. \quad (6)$$

Finally, on using wavenumber units (cm^{-1}), introducing the dimensionless quantity $x = h\nu/(kT)$ and taking into account that the excited level A_n is produced by two laser photons (Fig. 1), we get:

$$R_m = \frac{2\pi c}{F} (\sigma_i - \sigma_n)^3 \int_{\frac{hc}{kT} \sigma_n}^{\infty} \frac{1}{x(e^x - 1)} dx. \quad (7)$$

R_m is thus seen to be related to four parameters: the ionization potential σ_i of the ground state A_0 , the laser photon irradiance F , the ionization potential σ_n of A_n and, T the temperature of the resonance ionization cell.

Numerical Estimation of R_m

We now evaluate R_m by choosing parameter values and/or ranges which correspond to experimental conditions similar to those usually encountered in RIS and in particular as discussed in the introduction. A brief explanation of our choices follows.

The neutral atoms are produced in a cavity (oven), whose temperature T will be assumed to range from 1000 to 3000 K. Within these limits, a strong production of atoms in the vapor phase ($> 10^{10}$ atoms/ cm^3) is possible. This method of atomization of solid elements (even refractory ones) is widely used in RIS.

The atomic ionization potential of numerous elements is about 50000 cm^{-1} . This is particularly true for the lanthanides and the actinides (Th: 49000 cm^{-1} , Gd: 49500 cm^{-1} , ...). We will assume that our reference atom has an ionization potential σ_i of 50000 cm^{-1} .

The value of the ionization potential σ_n of the excited level A_n , considering a two-photon laser excitation process with an intermediate energy state, is an important parameter in the evaluation of R_m . With a laser, even of low radiance, one can easily saturate a level whose energy corresponds to twice the value of the laser photon energy. Based on our Gd studies, we shall evaluate R_m in the energy range from 2000 to

8000 cm^{-1} below the ionization threshold. The continuous scan of this range is easily achieved by using a single dye laser operating in the 21000 to 24000 cm^{-1} spectral range.

Finally, the radiance of typical pulsed lasers currently used in spectroscopy covers many decades. In the course of our study of the photoionization spectrum of Gd, an irradiance of $10^{23} \text{ cm}^{-2} \text{ s}^{-1}$ allowed us, as mentioned in the introduction, to observe a saturation spectrum. R_m will thus be calculated with an irradiance F , equal to this particular value.

Figure 2 shows R_m as a function of the ionization potential σ_n of the excited level A_n for various cavity temperatures. We observe therein that under realistic conditions, such as the ones assumed, the thermal photoionization process can indeed be substantially more important than laser photoionization.

To further quantify this point we solved the equation $R_m = 1$ for various σ_n values. Figure 3 shows the $R_m = 1$ curve on the σ_n, T plane. The fitting of this curve to a polynomial yielded:

$$\sigma_n = 2.721 T - 9.381 \cdot 10^{-5} T^2 + 1.351 \cdot 10^{-9} T^3. \quad (8)$$

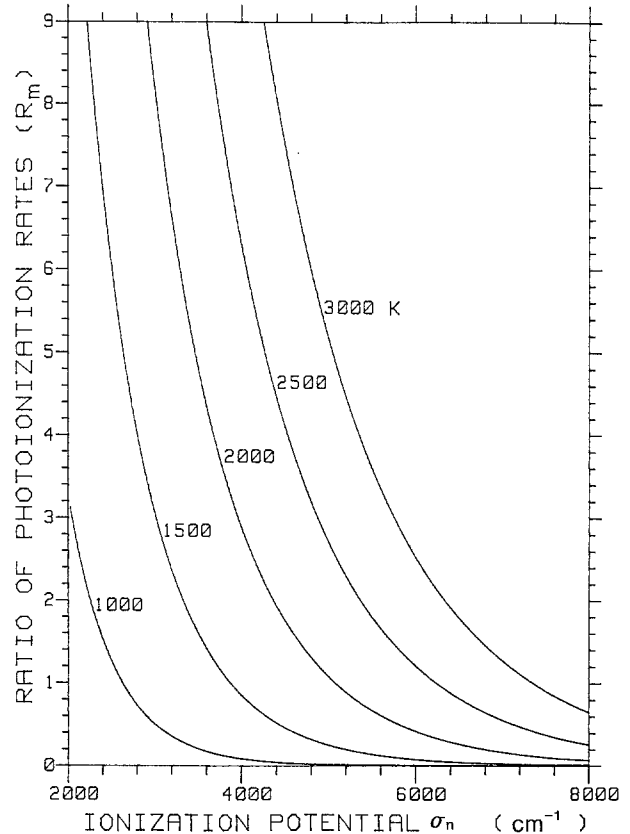


Fig. 2. The ratio R_m of thermal to photoionization rates as a function of the ionization potential σ_n of the excited (saturated) level A_n for various cavity temperatures, for an ionization threshold of 50000 cm^{-1} and a laser irradiance of $10^{23} \text{ cm}^{-2} \text{ s}^{-1}$

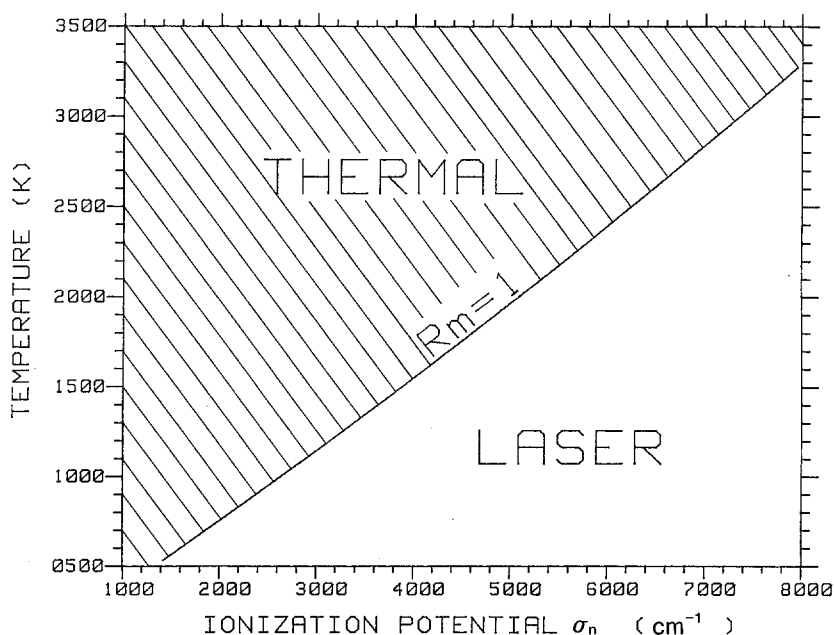


Fig. 3. The curve $R_m=1$ separates the two domains over which each of the photoionization processes dominates

From Fig. 3, one can clearly distinguish the domains over which each of the two photoionization processes dominates the other. For example, with a radiation cavity at 1000, 2000 or 3000 K we find, using (8), that the atomic population of energy levels as far as 2630, 5080 or 7350 cm^{-1} , respectively, below the ionization threshold are coupled to the continuum mainly through cavity radiation. That is to say, it is the laser radiation that leads to the selective excitation (saturation) of the discrete levels, but the coupling of the latter to the continuum is made through the radiation within the cavity and not through that of the laser. It should be pointed out that these discrete levels are relatively far from the ionization threshold.

Discussion and Conclusion

We now proceed with a discussion of the assumptions used. The influence of an atomic vapor source, based on the usual methods used in RIS, will be considered first. Next, the schematic atomic model used to obtain the R_m estimates will be improved by dealing qualitatively with the influence of levels near the excited level. Finally, the practical consequences of using the thermal radiation cavity concept in RIS will be presented.

The atomization cell and the irradiation region in a typical RIS system are sometimes separated. For instance, a furnace or a metal filament is often used in RIS to atomize the element under study. The irradiation region is then outside the furnace or in the proximity of the filament. In that case the thermal ionization rate (2) must be modified to include a

geometrical factor and the thermal emissivity of the heated surface. It should therefore be noted that the particulars of a given experimental setup could imply values of R_m different to the ones calculated herein.

Our calculation can be expanded by considering that there are many levels lying above and below the level which is excited by optical pumping. At high temperatures, the influence of thermal radiation can be pronounced. Thermal photons can produce not only photoionization but also induce a migration of the excited level towards other levels by absorption or stimulated emission processes. These diffusion effects have been investigated [13] for a temperature of 300 K. At higher temperatures, typical of RIS, the influence of the thermal field on the excited level will be more considerable. This phenomenon must be especially pronounced in lanthanides and actinides. Furthermore, when the excited level A_n is close to the ionization limit, the diffusion effects towards the ionization threshold can become important. This because the nearer the excited level to the ionization threshold, the higher the level density. In particular, the density of Rydberg states is much greater than the density of states below the excitation threshold. Hence one expects a preferential population migration towards Rydberg states and/or the ionization limit. It is important to note that migration towards Rydberg states must lead to increased thermal photoionization. One must then take into account this added photoionization process. Such a calculation is not easy. However, with the assumption that Rydberg atoms contribute directly to ion production, our estimation seems adequate for the calculation of a minimal value

of the relative efficiencies of thermal and laser photoionization.

The photoionization cross-section used in this work is accurate only for hydrogen-like atoms. The effective photoionization cross-section for complex elements, especially near the ionization threshold, is very likely greater than the value given by the hydrogen-like formula, as observed in studies on Gd and U [14, 15].

We now proceed to discuss a few consequences of this thermal effect on experimental RIS.

First, the resonant features in the spectra must be caused by the pumping effect of the laser. This because the thermal ionization is not a resonant process, since a continuous spectrum is coupled to the atomic system. Various pumping schemes that use intermediate resonant or quasi resonant levels are possible [16]. In these cases, it is relatively easy to saturate the upper level A_n of the transitions with a laser irradiance of the order of $10^{23} \text{ cm}^{-2} \text{ s}^{-1}$. When saturation of the level A_n is present, the intensity of the photoionization signal is independent of the intensity of the pump laser. This property can be used advantageously for the rapid identification of a thermally induced resonant ionization spectrum. We call such a spectrum a quasi-resonant ionization spectroscopy (QRIS) spectrum, since it differs from a spectrum whose photoionization is directly linked to the laser intensity. Moreover, this kind of spectrum has been observed, as mentioned in the introduction.

And second, thermal ionization can allow the study of a large number of highly excited levels using a single tunable pump laser. Using QRIS, one can access levels up to thousands of cm^{-1} below the ionization threshold.

Our results clearly indicate that under realistic experimental conditions, often met in RIS, thermal photoionization can dominate ionization via absorption of laser photons. We are currently involved in the

experimental investigation of these findings. The preliminary results are quite interesting. A full account of our experimental work will be the subject of a forthcoming communication.

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