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Absolute measurements of electron impact excitation cross-sections of atoms using cavity ringdown spectroscopy



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HIGHLIGHTS

- Cavity ringdown spectroscopy for electron impact excitation cross-sections.
- Measurements of absolute population densities of the energy levels.
- An analytical expression of electron impact excitation cross-section.
- The method is validated by two cases (the metastable Hg and the metastable Ne atoms).

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ABSTRACT

A new method of using cavity ringdown spectroscopy (CRDS) technique to measure apparent electron impact excitation cross-sections (EIECS) for different energy levels of an atom is described. The method involves measurements of absolute population densities of the energy levels in concern using the high sensitivity CRDS, leading to an analytical expression of EIECS as a function of the population densities. Determination of EIECS in this method does not require an external calibration. The proposed method is validated by determining EIECS of the metastable levels of Hg ($6s6p\ ^3P_0$) and Ne ($2p^53s\ ^3P_2$), and the results are in good agreement with the cross-sections reported in the literature. The population densities in both cases were extracted from the published data. This method exhibits promising potential for absolute measurements of EIECS of metastable energy levels.

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1. Introduction

Measurements of electron impact excitation cross-section (EIECS) of regular energy levels (optical transitions allowed) or metastable energy levels (optical transitions forbidden) are generally carried out with the electron energy loss technique, optical emission spectroscopy (OES) technique, or theoretical calculations (Phillips et al., 1981; Chutjian and Cartwright, 1981; Blum, 1981; Hanne et al., 1985; Filippelli et al., 1994). In 1981, C.C. Lin and group introduced a method based on laser induced fluorescence (LIF) spectroscopy along with OES to measure absolute EIECS of metastable levels. This method has remained to be one of the most extensively used experimental methods of measuring EIECS over the last 30 years though their latest advancement has evolved the method further to use OES only (Phillips et al., 1981; Jung et al., 2009). On the other hand, the conventional single-pass absorption spectroscopy technique, attempted once for EIECS measurements

has been abandoned and is not pursued these days (Milatz and Ornstein, 1935; Hadeishi, 1963; Mityureva and Penkin, 1983).

The measurement of EIECS using the LIF-OES method chiefly relies on measuring relative intensities of the emission lines (Phillips et al., 1981). The absolute EIECS is determined with the help of an external calibration process. Typically the method requires first to express the cross-section of a desired energy level in terms of a known excitation cross-section, emission line intensities, electron energy, etc. Then, a change in the emission line intensities is recorded with change in electron energy; consequently an excitation function is obtained. Afterwards, a known cross-section is used to determine the absolute EIECS of the desired energy level at the respective electron energies. This process requires not only emission line intensities to be measured, but also cross-section of another energy level to be known for the purpose of the calibration.

In our previous work (Wang et al., 2011), we introduced a new method to determine EIECS using cavity ringdown spectroscopy (CRDS) along with OES. The method involved solving a set of steady state population rate equations using the CRDS measured population density of one of the energy levels and the intensity

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ratio of two different emission lines. The experiments were conducted with an atmospheric pressure microwave plasma. The apparent EIECS of three energy levels of mercury (Hg), namely $6s6p\ ^3P_0$, $6s6p\ ^3P_1$, and $6s7s\ ^3S_1$, were determined simultaneously. The motivation of the previous work was to explore an alternative method of determining the absolute cross-sections using CRDS. In this work, we present a new version of the method that was described previously to measure EIECS of an atom (Wang et al., 2011). The present method is explained with a three energy level system, as an example. An analytical solution for EIECS has been derived from the steady state population rate equations; and the solution turns out to be a function of the population densities of the desired excited state and the ground state. Under the assumption that electron impact excitation is the dominant mechanism responsible for the density population of the energy levels, the population density of the excited level has a linear relationship to the ground state population density (Eq. 6). In such case, EIECS can be directly determined if the two population densities are known, i.e. in this case, experimentally determined by CRDS, and the method does not require an external calibration process. We applied the proposed method to determine EIECS in the two published cases: (i) EIECS of the $6s6p\ ^3P_0$ metastable level of Hg using data from our previous work (Wang et al., 2012) and (ii) EIECS of the $2p^53s\ ^3P_2$ metastable level of Ne with the data reported in the literature (Jung, 2010).

2. The method

The method is described with a three energy level system, as shown in Fig. 1. In this particular example, we assume that the energy level a and b are the two excited levels with the energy level a being metastable (optical transitions not allowed) and the energy level b is a regular excited level (optical transitions allowed). The ground state is represented by g . The target atoms, present in the ground state g , are exposed to a beam of mono-energetic electrons. As a result, some of the atoms in the ground state are excited to the higher energy levels a and b by the electron impact excitation mechanism. The metastable level a being optically forbidden does not radiate. However, the spontaneous transition $b \rightarrow a$ results in radiation at the wavelength λ . The atoms in the metastable level a is further pumped to the higher level b with a cavity ringdown laser beam at the wavelength λ .

Under the assumption that the excitation process is due solely to electron impact excitation mechanism and that the excited energy level de-excites to lower energy levels only through optical emission processes, namely spontaneous or stimulated emissions, at any given time the population rate equations for the energy

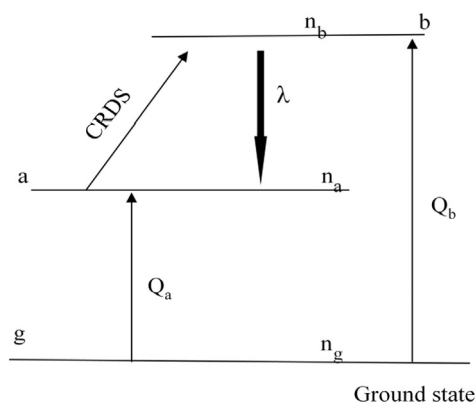


Fig. 1. Schematic of a general three-energy level system.

levels a and b can be given as (Phillips et al., 1981),

$$\frac{dn_a}{dt} = n_g \left(\frac{J}{e} \right) Q_a^{dir} + \sum_{j>a} j \neq b n_j A_{ja} + n_b A_{ba} - B_{ab} \rho(\nu) n_a + B_{ba} \rho(\nu) n_b - n_a A_a, \quad (1a)$$

$$\frac{dn_b}{dt} = n_g \left(\frac{J}{e} \right) Q_b^{dir} + \sum_{j>b} n_j A_{jb} + B_{ab} \rho(\nu) n_a - B_{ba} \rho(\nu) n_b - n_b A_b, \quad (1b)$$

where n_a , n_b , and n_g are the population densities in the energy levels a , b , and the ground state, respectively. The term (J/e) is the measure of electron flux in the electron beam, where J is the electron current density and e is the electron charge. A_{ij} and B_{ij} are the spontaneous and stimulated Einstein's coefficients corresponding to the lower energy level i and the upper energy level j . Similarly, the A_i 's represent the spontaneous Einstein's decay coefficient of the energy level i . $\rho(\nu)$ is the energy density of the laser beam at frequency ν .

Under the steady state condition, we have

$$n_g \left(\frac{J}{e} \right) Q_a^A + n_b A_{ba} - B_{ab} \rho(\nu) n_a + B_{ba} \rho(\nu) n_b - n_a A_a = 0, \quad (2a)$$

$$n_g \left(\frac{J}{e} \right) Q_b^A + B_{ab} \rho(\nu) n_a - B_{ba} \rho(\nu) n_b - n_b A_b = 0, \quad (2b)$$

where $Q_a^A = Q_a^{dir} + \sum_{j>a, j \neq b} Q_{ja}$ is known as the apparent cross-section for the energy level a , with the cascaded term $\sum_{j>a, j \neq b} n_j A_{ja}$ replaced by $n_g (J/e) \sum_{j>a, j \neq b} Q_{ja}$, where the terms in summation are known as the optical cross-sections. From Eq. (2) we have

$$n_a = \frac{n_g (J/e) [Q_a^A + (Q_b^A A_{ba} + B_{ba} \rho) / (A_b + B_{ba} \rho)]}{A_a + B_{ab} \rho - (B_{ab} \rho (A_{ba} + B_{ba} \rho) / (A_b + B_{ba} \rho))} \quad (3)$$

In a CRDS experiment, more than 99% of the incident laser power is reflected back, and only a fraction ($< 1\%$) of the beam energy interacts with the absorbing molecules inside the cavity. This results in a significant reduction in the magnitude of the term $B_{ab} \rho$ inside the cavity in comparison to outside the cavity.

In our CRDS system, the ringdown laser beam from the optical parametric oscillators (OPO) system at 404.65 nm has a typical photon density outside the cavity of on the order of 10^{17} photons $\text{cm}^2 \text{s}^{-1}$, corresponding to the beam energy of $B_{ba} \rho \sim 10^4 \text{ s}^{-1}$ inside the cavity. So are for the other CRDS systems, the beam energy inside a ringdown cavity remains approximately on the same order. Typically, the spontaneous emission rates (Einstein's constant A) A_b and A_{ba} are on the orders of 10^8 and 10^7 s^{-1} , respectively [NIST Atomic Database]. Therefore, in a CRDS measurement we can consider

$$A_b + B_{ba} \rho \approx A_b \quad \text{and} \quad A_{ba} + B_{ba} \rho \approx A_{ba}$$

Therefore, Eq. (3) is modified to be

$$n_a = \frac{n_g (J/e) (Q_a^A + (Q_b^A A_{ba} / A_b))}{A_a + B_{ab} \rho (1 - (A_{ba} / A_b))}. \quad (4)$$

Since the optical transition cross-section from the energy level b to a is given as $Q_{ba} = (Q_b^A A_{ba} / A_b)$,

Eq. 4 can be further modified to

$$n_a = \frac{n_g (J/e) (Q_a^A + Q_{ba})}{A_a + B_{ab} \rho (1 - (A_{ba} / A_b))} \quad (5)$$

Note that the aforementioned definition of Q_a^A , i.e. $Q_a^A = Q_a^{dir} + \sum_{j>a, j \neq b} Q_{ja}$, does not include the optical cross-section term Q_{ba} . Therefore, the term $(Q_a^A + Q_{ba})$ in Eq. (5) is actually the total apparent cross-section of energy level a , denoted as Q_a^{App} .

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