Multiphoton excitation of autoionizing states of Mg: Line-shape studies of the $3p^2\,{}^1S$ state

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We have observed ionization of Mg by both direct and stepwise two-photon excitation of the $3p^2\,{}^1S$ state. The line shape of the single-color direct process is strongly modified by the resonance denominator associated with the intermediate virtual state. The measured energy and width of this resonance as determined by the stepwise two-color technique agree well with previous determinations.

This paper reports some experiments on two-photon ionization of Mg at wavelengths $\lambda \sim 300$ nm, a process which results in a Mg^+ ion in its ground state $3s\,{}^2S$ and an ejected electron of energy $\sim \frac{3}{4}$ eV. In this energy range lies the lowest autoionizing state of Mg, the $3p^2\,{}^1S$ state, which was first observed in photoionization by Bradley *et al.*,[1] and which has since been seen in ejected-electron spectroscopy,[2] electron-impact excitation,[3] and optical-emission spectroscopy.[4] The general goal of our work is to obtain accurate spectral information on doubly excited states of light atoms, which at present is largely unavailable. The specific purposes of this paper are, first, to report our determination of the resonance parameters of Mg $3p^2\,{}^1S$; when these are combined with the results of previous experimental and theoretical work, the ^1S state can be regarded as one of the best-characterized autoionizing states of the alkaline-earth metals. Second, we wish to draw attention to Mg as a candidate for approximate realization of an important case of multiphoton ionization: a three-level system including an autoionizing state, with nearly equal energy intervals between the states. Our experiments have been carried out in a laser intensity regime in which the ionization line shape can be understood in terms of perturbation theory, but future work at higher intensities may reveal predicted effects[5,6] of strong coupling.

We utilize a resonance ionization mass spectrometry (RIMS) apparatus which has been described in detail elsewhere.[7] A schematic diagram is shown in Fig. 1. A resistively heated filament produces a rarefied atomic vapor in the source chamber of a mass spectrometer. For these experiments, we manufacture the filament from a piece of magnesium ribbon approximately $1.5\times10\times0.2$ mm^3 in size. The filament is operated at a temperature of 600 °C. Ions are produced by absorption of ultraviolet radiation from one or two frequency-doubled, Nd:YAG-pumped dye lasers (YAG denotes yttrium aluminum garnet). These ions are focused and accelerated to approximately 6500 V. We use a 90°, 30-cm magnetic sector to separate ions according to mass. The ^{24}Mg ions are then detected using a 17-stage Cu-Be particle multiplier. The output is amplified and directed to a gated boxcar integrator synchronized to the lasers. The integrated signal is read by a digital voltmeter which is interfaced with a laboratory computer. Data acquisition is controlled by the computer which also controls scanning the laser wavelength. We determine the absolute wavelength in these experiments using a 0.4-m spectrometer calibrated with several emission standards as a laser wavemeter. The uncertainty in the wavelength is estimated to be 0.004%.

These experiments differ from those previously reported by our group[7,8] in that for the two-color, stepwise excitation scheme we employ two Nd:YAG-pumped dye laser systems, both of which are frequency doubled in potassium dihydrogen phosphate (KDP) crystals. A master clock synchronizes the two lasers and the delay of each may be independently varied over a range of 10 μsec. These lasers produce pulses at a repetition rate of 10 Hz, which are 7 nsec in duration and have a linewidth of approximately 1 cm^{-1}. Both lasers are vertically polarized.

The mass spectrometer virtually eliminates the possibility of detecting ions other than $^{24}Mg^+$ which may be present as impurities in the sample. An instrumental throughput of greater than 50% is routinely attained and a detection efficiency of unity is well within the capability of the apparatus.

The first results we discuss involve stepwise excitation of the $3p^2\,{}^1S$ state:

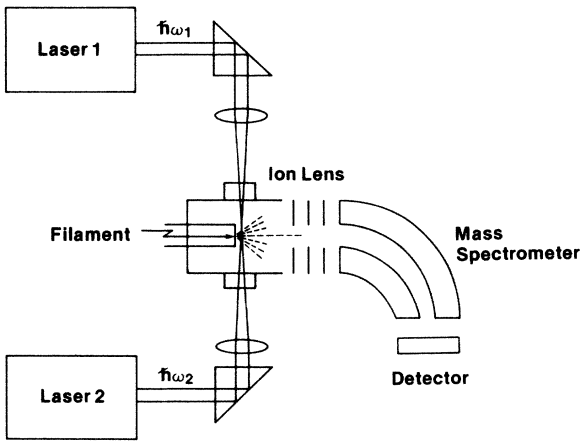

FIG. 1. Schematic RIMS apparatus.

$$\text{Mg } 3s^2+\lambda_1(285.3\text{ nm})\rightarrow 3s\,3p\ ^1P^\circ\ ,$$
$$3s\,3p\ ^1P^\circ+\lambda_2(\sim 300\text{ nm})\rightarrow 3p^2\ ^1S\ , \quad (1)$$

where λ_1 is fixed and λ_2 is scanned. This is the same scheme as used by Bradley *et al.*,[1] except that we detect Mg^+ ions rather than photoelectrons (earlier work of Bradley *et al.* also measured photoabsorption by the $^1P^\circ$ state, as discussed in Ref. 1 and references therein). Relative timing of the pulses from the two lasers was measured by a fast ($\sim$1-nsec rise time) photodiode. Maximum ionization was obtained when the two pulses were simultaneous to within the resolution of the photodiode, and the data reported here were accordingly obtained under conditions of zero time delay. The laser intensities are approximately 10^6 W cm^{-2}. The ion signal $I(\lambda)$ as a function of the wavelength λ_2 is shown in Fig. 2.

We have analyzed the data of Fig. 2 in terms of the Fano profile formula:[9]

$$I(\lambda)\equiv I(\varepsilon)=I_B+I_R(q+\varepsilon)^2/(1+\varepsilon^2)\ , \quad (2)$$

where $\varepsilon=2(E-E_0)/\Gamma$, with E_0 being the energy of the resonance and Γ its width. The background ion signal I_B derives from direct photoionization of the $^1P^\circ$ state into the $3s\varepsilon d$ continuum. This signal varies slowly over the wavelength range of our scan, and we have found that it is adequately represented by a linear energy dependence: $I_B=I_0+I_1\varepsilon$. A least-squares fit of the six parameters, I_0, I_1, I_R, q, E_0, and Γ, gives the solid curve shown in Fig. 2 and the values in Table I.

Our results for the energy and the width of the resonance are in very good agreement with those reported by Bradley *et al.*[1] It should be noted that a Lorentzian fit (i.e., $q=\infty$) to the resonance profile was made in Ref. 1, which could in principle result in different values of E_0 and Γ. However, the asymmetry of the profile is sufficiently small that any such differences are less than the experimental uncertainties. On the other hand, the slightly lower value of $E_0=68\,150$ cm^{-1} reported by Rassi *et al.*[2] may be due to an effect of profile asymmetry. The energy cited in Ref. 2 is that of a sharp maximum in the electron impact ionization spectrum of the ground state of Mg, which would be characterized by a value of q which, since it is dependent on the excitation process, will in general be different from that of photoionization of the $^1P^\circ$ state. A simple analysis of Eq. (2) shows that the maximum occurs at an energy $E=E_0+\Gamma/2q$. The energy reported in Ref. 2 is within a half width of ours, so there may be no real discrepancy with the present results.

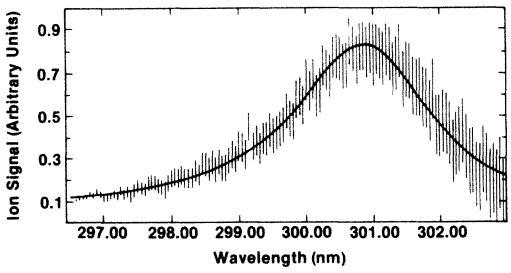

FIG. 2. Ionization signal as a function of λ_2 for the stepwise excitation scheme of Eq. (1). Solid line indicates fit to Fano profile of Eq. (2).

Theoretical calculation of the $3p^2\ ^1S$ state is evidently a delicate matter, as shown in Table II. Most results of which we are aware come from calculations in the close-coupling approximation. The results of Burke and Moores[10] and of Mendoza[11–13] together provide an interesting example of the convergence of close-coupling results as the number of ion target states is increased. Table II shows that the energy becomes progressively closer to the experimental value as the number of target states is increased from two to eight. The width, on the other hand, shows irregular behavior and appears to be converging to a value about one-third higher than the experimental one. We do not know of any published calculated values of q. However, all calculations[12,13,15] of the photoionization cross section of the $^1P^\circ$ state show the ^1S resonance as a nearly symmetric feature, indicating a high value of q. The absolute cross section was also measured by Bradley

TABLE I. Values of the resonance parameters of Eq. (2): comparison of energy and width with other measurements. The uncertainties in our values derive from uncertainties in wavelength measurement and from statistics of the fit. The uncertainties in the other values are derived by us from presuming unit uncertainty in the last digit cited by the original authors. ($I_0/I_1=9.1$; $q^2I_R/I_0=29.6$.)

Parameter	Present work	Ref. 1	Ref. 2	Ref. 3	Ref. 4
q	24.4±1				
E_0 (cm^{-1})	68 268±4	68 275±11	68150±80	a	68 275±11[b]
Γ (cm^{-1})	278±8	276±11			

[a] Feature visible in electron energy loss around 8.5 eV, consistent with other values. No measured value reported by authors.

[b] Feature observed in emission spectrum of a Mg plasma, at 300.9 nm corresponding to $3p^2\ ^1S-3s\,3p\ ^1P^\circ$ transition.

TABLE II. Calculated energies E and widths Γ of the $3p^2\,{}^1S$ state of Mg. Values are in rydbergs; the energy is expressed in terms of binding energy with respect to Mg^+ $3p$ (center of gravity). CC, close coupling; CCP, close coupling with polarization potential. Numbers within parentheses after the experimental values indicate the uncertainties in the final digit(s).

Method	E	Γ ($\times 10^3$)
Two-state CC[a]	0.1936	3.30
Three-state CC[a]	0.2503	1.25
Three-state CCP[b]	0.2530	
Four-state CCP[b]	0.2574	3.17[c]
Eight-state CCP[d]	0.2611	3.49
Feshbach method[e]	0.266	3.7
Expt. values		
Ref. 1	0.2654(1)	2.52(10)
This work	0.2655(1)	2.55(7)

[a] Reference 10.
[b] Reference 11.
[c] From Ref. 12.
[d] Reference 13.
[e] Reference 14.

et al., with an uncertainty of about 50%. A review by Mendoza[12] of experimental and theoretical values of the absolute cross section shows that significant discrepancies exist between them. Unfortunately our results cannot be placed on an absolute basis.

The second part of this report concerns the two-photon ionization of Mg by a single laser, as a function of wavelength over a range which includes the resonance excitation $3s^2 \rightarrow 3p^2\,{}^1S$. A similar scheme was used previously[8] on the analogous $2s^2$-$2p^2$ transition of Be. Figure 3 shows a broad scan of the ionization signal as a function of wavelength. This trace has not been normalized with respect to the laser intensity, which varies somewhat over the scan due to changes in the dye gain curve, but the average intensity is approximately 10^6 W cm^{-2}. The peak at 285.3 nm is of course due to two-photon ionization via the ${}^1S \rightarrow {}^1P^\circ$ resonance transition. The two-photon $3s^2$–$3p^2\,{}^1S$ transition can be seen as a weak feature in the red wing of this peak.

Figure 4 shows the $3p^2$ feature properly normalized to

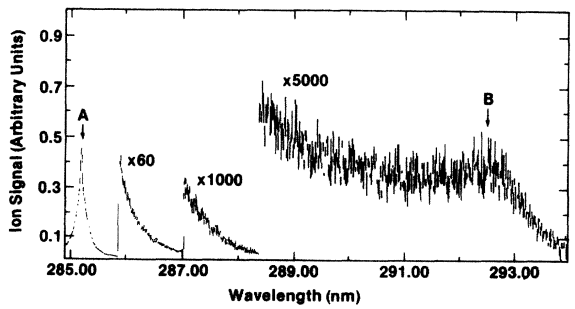

FIG. 3. Broad scan of ionization signal as a function of wavelength for irradiation by a single laser. This range includes resonance ionization via one-photon excitation of the $3p$ state (285.3 nm) and two-photon excitation of the $3p^2$ state (293 nm).

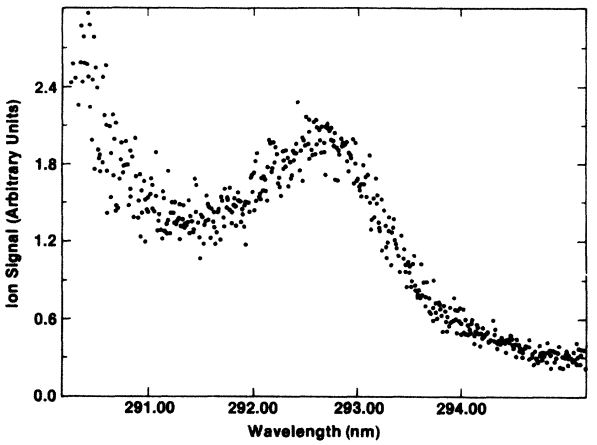

FIG. 4. The $3p^2$ feature as in Fig. 3, with laser intensity held constant as wavelength is varied.

the dye gain curve so that the laser intensity is effectively constant as a function of wavelength. Unlike the trace of Fig. 2, the line shape is obviously non-Lorentzian. We believe it can be described by a fairly simple model, which is the weak-intensity limit of systems discussed in Refs. 5 and 6.

We consider the expression for the rate σ_{gf} of two-photon transitions from a ground state $|g\rangle$ to a final state $|f\rangle$, as given by perturbation theory:[5]

$$\sigma_{gf} \sim \left| \sum_i \frac{D_{gi} D_{if}}{\nu - \nu_i} \right|^2 , \tag{3}$$

where ν is the wave number of the photon, D_{ij} the matrix element $\langle j | D | i \rangle$ of the electric dipole operator, and the sum is taken over all states $|i\rangle$ with energies $hc\nu_i$. In our case this sum is dominated by the contribution from the state $3s\,3p\,{}^1P^\circ(m_J=0)\,|\,3p\rangle$; in the vicinity of the two-photon transition to the $3p^2$ state, $|\nu-\nu_i| \sim 900$ cm^{-1}, whereas the nearest other state in this sum, $3s4p\,{}^1P^\circ$, lies at $|\nu-\nu_i| \sim 15\,000$ cm^{-1}. (In addition, oscillator strength data[16] indicates that $|D_{g4p}/D_{g3p}| \sim 0.3$.) Reducing Eq. (3) to the contribution from $|3p\rangle$ only, we have

$$\sigma_{gf} \sim \left| \frac{D_{g3p}}{\nu - \nu_{3p}} \right|^2 |\langle f | D | 3p \rangle|^2 . \tag{4}$$

The total ionization rate $I_g(\nu)$ will be given by $\sum_f \sigma_{gf}$, the sum including the autoionizing channel with the $3p^2\,{}^1S$ resonance[9] and the photoionization continuum associated with the $3s\varepsilon d$ configuration. Since only the rightmost term of Eq. (4) depends upon f, this summation just reproduces the photoionization cross section of the $3p$ state, and we obtain

$$I_g(\nu) = A(\nu - \nu_{3p})^{-2} I(\varepsilon) , \tag{5}$$

where A is constant and $I(\varepsilon)$ is given by Eq. (2). Figure 5 shows the product $(\nu-\nu_{3p})^2 I_g(\nu)$. To within experimental uncertainty (and a normalization factor that we have not determined independently) this is the same as the ion signal of Fig. 2.

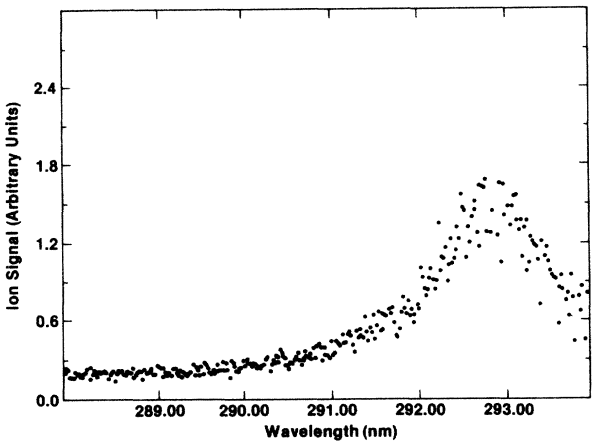

FIG. 5. The signal of Fig. 4 multiplied by the detuning factor $(\nu-\nu_{3p})^2$. The Fano line shape is recovered.

For the laser intensities utilized in this experiment it thus appears that the autoionizing line shape is given by the usual profile formula modulated by the Lorentzian wing of the one-photon resonance transition. However, it may be possible to produce departures from this simple behavior by increasing the power. For instance, broadening the main resonance of Fig. 4 would effectively move the $3p^2$ feature further up onto its shoulder. Novel effects are predicted[5,6] to occur as a result of strong radiative coupling between a discrete and an autoionizing state. We have not carried out such experiments at present, but it is hoped that publication of these first results will stimulate independent interest.

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