Angular distributions of ejected electrons from autoionizing 3pnd states of magnesium

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We have measured the angular distributions of electrons ejected from doubly excited autoionizing Rydberg 3pnd J = 1 and 3 states of magnesium, where n = 10–18. To excite the aligned 3snt 1D2 states of Mg, we used two dye lasers crossed with an atomic beam. A third laser, linearly polarized in the same direction as the other two, excited the atoms in the 3snd states to the 3pnd states. The angular distributions of ejected electrons are given by \( \frac{d\sigma}{d\Omega} = \sum_k a_k P_k(\cos \theta) \), where \( k = 0, 2, 4, 6 \). We measured the angular distribution parameters \( a_k \) as a function of the energy of the third laser photon using an electron detector and a Mg+ ion detector. We compare our results with the predictions of an R-matrix multichannel quantum-defect theory. We find good agreement between experiment and theory.

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I. INTRODUCTION

The \( R \)-matrix method, when combined with multichannel quantum-defect theory (MQDT) [1], has been used with extraordinary success in predicting the photoabsorption cross sections of alkaline-earth atoms in the energy range up to about 5 eV above the lowest ionization limit; an energy range that includes autoionizing states converging to low-lying excited states of the ion. The calculated photoabsorption spectra agree with both the vacuum-ultraviolet spectra from the ground-state and isolated-core-excitation spectra from bound Rydberg states [2–17]. A more stringent test of the calculations is to measure the angular distributions of the ejected electrons from autoionizing states, and several comparisons of this sort have been made [3–5, 7, 8, 10–19], all between measured and calculated angular distributions of electrons resulting from the excitation of bound Rydberg msns 1S0 states to autoionizing mpsn J = 1 states. The agreement for angular distributions is reasonably good, but not as good as in the case of the photoabsorption spectra. A review of experimental and theoretical work done up to 1988 may be found in Ref. [20].

Here we report the measurements of the angular distributions of electrons ejected from Mg 3pnd autoionizing states. Using two lasers linearly polarized in the same direction, an aligned sample of Mg 3snd 1D2 atoms is produced. These atoms are further excited by a laser linearly polarized in the same direction to the 3pnd J = 1 and 3 autoionizing states. In this case the Mg+ ion is left in the 3s_{1/2} state and the departing electron can be in either the epj or efj continuum. This paper reports measurements and theoretical predictions in Mg of the higher-order angular distributions achieved by exciting an aligned, nonspherically symmetric Rydberg state to autoionizing states. The measured angular distributions are compared to those calculated using the \( J = 1 \) and 3 \( K \) matrices, which give an excellent representation of the photoabsorption spectrum. As we shall see, the agreement between theory and experiment is good, but not quite as good as in the case of the photoabsorption line shape. These measurements provide useful insight into the validity of important MQDT calculations of other properties of Mg, such as its dielectronic recombination rate in a plasma [21].

In the following sections of the paper we present our experimental method, the theory, the experimental and theoretical results, and a discussion of the results. The Appendix contains an independently derived, alternative formulation of the theory.

II. EXPERIMENTAL METHOD

Our excitation scheme is shown in Fig. 1. The first laser photon excited one electron from the Mg ground state to the lowest excited state: 3s3s 1S0 \( \rightarrow \) 3s3p 1P1. The second photon excited the same electron to a bound 3snd 1D2 Rydberg state just below the ionization potential. Both photons were linearly polarized in the same direction, producing m = 0 levels, where m is the azimuthal orbital angular momentum quantum number. The wavelength of the second laser was tuned over a range 375–400 nm to produce various n levels n = 10–18 of the Rydberg d state. The energies of the 3snd 1D2 states are given in Ref. [22]. The first two lasers were used solely to produce the aligned 3snd 1D2 state. These lasers were fixed in frequency while measuring spectra of the autoionizing 3pnd states. The third and last linearly polarized photon excited the inner electron transition 3snd \( \rightarrow \) 3pnd, producing the autoionizing state [23]. To conform to conventional descriptions we shall call the 3snd state \( |J_0\rangle \); its total angular momentum is \( J_0 = 2 \). The autoionizing 3pnd state has \( J = 1 \) or 3. The 3pnd levels converge to the two 3p Mg+ ion levels that have a
fine-structure splitting of 92 cm\(^{-1}\). Due to the finite widths of the 3pd levels and the small Mg\(^+\) 3p fine-structure interval, transitions to 3pd levels converging to both 3p\(_{1/2}\) and 3p\(_{3/2}\) limits overlap and the third photon excites both of them. The transitions to \(J = 1\) and 3 levels overlap also. We tuned the third laser over a range of \(\sim 300\) cm\(^{-1}\) centered on the ionic 3s\(_{1/2}\)\(\rightarrow\)3p\(_{1/2}\) and 3p\(_{3/2}\) transitions, and measured the angular distributions of the ejected electrons as described below.

Each photon came from a dye-laser oscillator and amplifier, the output of which was doubled in an angle-tuned potassium dihydrogen phosphate crystal. A tracking device maintained the phase-matching angle of the third laser’s doubling crystal as the third laser was tuned. The dye lasers were pumped by a pulsed neodymium-doped yttrium aluminum garnet (Nd:YAG) laser operating at a 20-Hz repetition rate. Each laser pulse had a pulse length of about 5 ns and a frequency width of about 1 cm\(^{-1}\). The collinear laser beams crossed a thermal atomic beam of Mg at right angles. A diagram of our optical apparatus and detectors can be found in Fig. 2.

The first and second lasers entered the vacuum chamber from the left side of Fig. 2. Both passed through a uv-grade double Fresnel rhomb and linear polarizer to ensure that they were highly linearly polarized in the same direction. The double Fresnel rhomb functioned as an achromatic half-wave plate, allowing the initial polarization of the lasers to be rotated to any angle without loss of intensity. The linear polarizer after the rhomb was rotated to pass the rhomb’s output and to ensure that the purity of the linear polarization was at least 100:1.

The third laser beam entered the vacuum chamber from the right side of Fig. 2, collinear to the first two. It passed through a similar polarization controller. The polarizations of all of the laser beams were always set to point in the same direction as the angle was varied. We found that the vacuum chamber windows had no effect on the laser polarization direction or purity.

A portion of the undoubled third laser beam was split off and sent into an Ar optogalvanic cell, which provided absolute frequency reference markers [24]. Another portion was sent through an etalon, providing fringes 4 cm\(^{-1}\) apart. These two signals were recorded simultaneously with all of our Mg spectra, giving us an absolute frequency calibration and a means of linearizing the scan of the third laser.

Our detectors, shown schematically in perspective in Fig. 2, consisted of an ion detector and an electron detector, each directly above or below the laser–atomic-beam interaction point. The line through this point and the detectors was perpendicular to the plane of the laser beams and atomic beam to within two degrees. Each detector was made of a stacked pair of microchannel plates (MCP’s) biased with 2000 V of the appropriate polarity to detect positive ions or electrons. The MCP’s were mounted at the back of a 10-cm-long tube to provide energy analysis and angular resolution for the electron detector. The negative high voltage at the face of the ion detector was completely shielded from the laser–atomic-beam interaction point by two grounded grids. A pair of grids parallel to the laser and atomic beams surrounded the laser–atomic-beam interaction point. These grids were kept grounded during the laser pulses. After about 1 \(\mu\)s, a brief high-voltage pulse was applied to force the entire slow-moving cloud of Mg\(^+\) ions resulting from autoionization of the Mg 3pd atoms to the ion detector. By the time the ion extraction pulse was applied, the electrons had already hit their detector. Time-of-flight energy analysis of the electron signal was necessary since the Mg atoms could be photoionized by absorbing two 285-nm photons from the first laser alone. This produced relatively low-energy photoelectrons, which arrived at the detector about 20 ns after the high-energy electrons emitted from the autoionizing 3pd Mg states appeared at the detector. The electron pulses were only 2 or 3 ns long, so we could easily temporally resolve the two signals. The second electron pulse, having nothing to do with the 3pd states, was eliminated entirely by using a gated integrator, which closed well before the second pulse arrived.

The electronics used to process the signals were the same as those described in detail in Ref. [19]. In brief, the MCP’s amplified the electrons or ions by about 10\(^6\). A separate fast amplifier brought the signals up to the

![FIG. 1. Energy-level diagram for the three laser excitation of the 3pd states of Mg. The first laser is fixed in frequency and excites the “outer” electron. The second laser excites the outer electron to a Rydberg state, with a particular \(n\) value in the range 10–18. The third laser excites the “inner” electron, and is tuned over a several-hundred-cm\(^{-1}\)-wide region centered on the autoionizing 3pd resonances. All of the lasers are linearly polarized in the same direction. The angular distribution and line shape of the third transition are measured as a function of the tuning of the third laser. The 3pd states are split by the 92 cm\(^{-1}\) fine-structure splitting of the excited ion core.](image-url)
1 V level as soon as they exited the vacuum chamber. Gated integrators triggered by the laser pulses converted the signals to slowly varying dc levels. The gate width and delay were much greater for the ion pulses than for the electron pulses, since the ions traveled more slowly to their detector. An analog-to-digital converter and computer measured and recorded the electron and ion dc signals along with the Ar optogalvanic lines and étalon fringes for further analysis. To minimize distortions of the angular distributions, the entire region surrounding the path of the autoionized electrons was sprayed with graphite powder to reduce stray electric fields and was enclosed with two layers of μ metal to reduce stray magnetic fields.

The specific autoionizing Rydberg states we measured are 3pnd, excited by one photon from 3snd states. Symmetry considerations and angular momentum selection rules constrain the angular distribution to be of the form

\[
\frac{d\sigma}{d\Omega} (\theta) = \frac{I_0}{4\pi} \left[ 1 + \beta P_2(\cos\theta) + \gamma P_4(\cos\theta) + \epsilon P_6(\cos\theta) \right],
\]

where \(I_0\) is the total integrated cross section, \(P_k(\cos\theta)\) is the \(k\)th Legendre polynomial, and \(\theta\) is the polar angle between the laser polarization and the direction of the emitted electron. The parameters \(I_0\), \(\beta\), \(\gamma\), and \(\epsilon\) are any real numbers. \(I_0\) as a function of energy gives the total photo-absorption cross section, or line shape, of the transition. The three angular parameters \(\beta\), \(\gamma\), and \(\epsilon\) vary as a function of energy; together they constitute the three parameter “spectra,” which we measure and calculate in this paper.

To ensure that we were obtaining the expected angular distribution, we fixed the energy of all lasers and rotated the laser polarization under the electron detector 360° in increments of 10°. Since the ion signal does not depend on \(\theta\), we used any changes in it to correct the electron signal for changes in laser intensity and alignment during the measurement. To correct the electron signal, we simply divided it by the ion signal. Figure 3 shows the graph
of the corrected electron signal versus $\theta$ for the $3p_{10}d$ state with the doubled third laser set at 35 660 cm$^{-1}$. The error bars show the 1$\sigma$ error of the quotient, Gaussian propagated from the electron and ion signal Poisson errors. The solid line in Fig. 3 is the fit of Eq. (1) to these data points. The fit is quite good, and clearly the angular distribution is as expected. This fit gives precise numerical values for $\beta$, $\gamma$, and $\epsilon$; these will be discussed later in this section. All of Fig. 3 corresponds to only one energy point in the spectra of $\beta$, $\gamma$, and $\epsilon$. In principle, the procedure used to produce Fig. 3 could be repeated thousands of times with a slightly different third laser energy each time to produce parameter spectra as a function of photon energy.

We chose instead to use one electron detector at a particular angle, tuned the laser over the energy range, then changed the detector to another angle and tuned the laser again over the same range. For one particular $3p_{nd}d$ state, we typically took electron spectra at ten different angles $\theta$, ranging from $\theta=0^\circ$ to $\theta=90^\circ$. Since the expected angular distribution is even about $\theta=0^\circ$ and periodic with period 180$^\circ$, measuring on the interval $[0^\circ, 90^\circ]$ was all that was needed. At each energy point, we fit Eq. (1a) to the ten different electron signal values corresponding to each of the ten angles. At each energy point this produced fitted values for $\beta$, $\gamma$, and $\epsilon$, thus providing angular distribution parameter spectra over the same energy range.

The problem with this procedure was that over the approximately five hours it took to collect ten electron spectra, the signal strengths would change due to unavoidable shifts in the lasers’ power and alignment. These changes would mean that a comparison of electron signals taken at the beginning and end of the data-taking run would be meaningless, and a fit to them would give wrong results.

The ion signal, which does not depend on $\theta$, was used to correct for these electron signal shifts. In principle, each ion signal, taken simultaneously with each electron signal, should be the same, regardless of $\theta$. In practice, the ion signals varied according to the laser power and alignment. We divided each electron signal value at each energy point by the ion signal value taken simultaneously. Any fluctuation in the laser power or alignment would affect the electron and ion signal values in the same way. Taking the quotient cancels the fluctuations. This method of dividing the electron signal by the simultaneous ion signal also has the advantage of eliminating any effect due to varying optical saturation of the transition. Optical saturation, whether strong or weak at a particular energy, affects the electron and ion signal by the same factor, and so the effect cancels in the quotient.

The quotient can be written as

$$\frac{d\sigma}{d\Omega} = \frac{I_0}{4\pi} = a_0 + a_2P_2(\cos\theta) + a_4P_4(\cos\theta) + a_6P_6(\cos\theta),$$

(1b)

since the ion signal is proportional to the total cross section $I_0$. Both sides of Eq. (1b) still contain an a priori unknown overall experimental normalization factor, due to the arbitrary experimental units of $d\sigma/d\Omega$ and $I_0$. Thus in general the fitted value of $a_0$ is not 1.0. The fitted value of $a_0$ determines the overall normalization. This normalization can be removed by taking the quotients $\beta = a_2/a_0$, $\gamma = a_4/a_0$, and $\epsilon = a_6/a_0$ since the same normalization factor is contained in $a_0$, $a_2$, $a_4$, and $a_6$.

The above procedure for normalizing the electron signals assumes that the relative efficiency of the electron and ion detector systems remained constant over the approximately five hours of a data-taking run. We thoroughly warmed up the apparatus and left the gate positions and widths, MCP voltages, and amplifier gains unchanged. The one uncontrollable efficiency factor was the intrinsic gain of the MCP’s themselves, which did change over the space of some weeks. To confirm that this did not vary significantly during a data-taking run, we measured the $\theta=0^\circ$ electron signal at the beginning and end of each data-taking run, and several times in between the scans at other $\theta$’s. We saw that the ratio of the electron signal at $\theta=0^\circ$ to the ion signal did not change over the entire data-taking run.

For the fitting algorithm to work properly, the zero offset of the dc output of the gated integrators had to be adjusted so that the output was zero when a true zero signal occurred. Otherwise, in the case of a small signal plus a large zero offset, the fitting algorithm would interpret it as a large signal, and give erroneous results. For each scan, we carefully adjusted the zero offset to be less than 0.005 V out of a 5-V full scale signal. When the true signals fell to about 0.05 V, this uncertainty in the zero offset rendered our results meaningless. This effect limited us to scanning within about $\pm$200 cm$^{-1}$ of the signal peak; in this energy range the signals were always at least 0.05 V.

For fitting purposes we used Eq. (1b), which is linear in the four fitted parameters $a_0$, $a_2$, $a_4$, $a_6$. We used the singular value decomposition method, as described in Ref. [25], to fit Eq. (1b) to the ten quotients of electron signal to simultaneous ion signal. The ten data points were taken at the ten different values of $\theta$ corresponding to one energy value. A separate fit was performed for each doubled third laser photon energy value in the range, producing fitted spectra of the $a_0$, $a_2$, $a_4$, and $a_6$ parameters. As expected, we found that the fitted values for $a_0$ were nearly constant as a function of energy. The actual fitted angular distribution parameters $\beta$, $\gamma$, and $\epsilon$ were obtained from $\beta = a_2/a_0$, $\gamma = a_4/a_0$, and $\epsilon = a_6/a_0$.

To show that the above procedure (method A) for fitting the ten electron signal spectra at the ten different angles $\theta$ to produce parameter spectra is valid, we measured the electron signal as a function of $\theta$ by manually rotating the laser polarizers, with the energies of all of the lasers fixed (method B). We then fit the resulting angular distribution to Eq. (1), as shown in Fig. 3. This fit gave values for the parameters $\beta$, $\gamma$, and $\epsilon$, shown in the row for method B in Table I. Selecting the values of $\beta$, $\gamma$, and $\epsilon$ at that same single energy point from the $3p_{10}d$ parameter spectra gives the values for $\beta$, $\gamma$, and $\epsilon$ shown in the row for method A in Table I. Method B is the more traditional way to obtain angular distributions, but as our errors in the method A parameter values are about 0.5 (as we shall discuss later), the two methods are equally valid.
TABLE I. Comparison of measured values of angular distribution parameters of the 3p 10d state at 35 660 cm\(^{-1}\). Method A is used for the parameter spectra shown in this paper. It involves scanning the third laser energy to get electron signal spectra at ten different angles \(\theta\), then fitting those ten data points to Eq. (1) to obtain the \(\beta\), \(\gamma\), and \(\epsilon\). The row for method A shows just one energy point out of many from the 3p 10d parameter spectra obtained in this manner. Method B involves fixing the energies of all of the lasers, then manually rotating the polarization of all of them to vary \(\theta\). We obtain the graph shown in Fig. 3, then fit to Eq. (1) and obtain \(\beta\), \(\gamma\), and \(\epsilon\) at a single energy. The good agreement between the two methods shows that both are equally valid. For comparison the theory values derived in Sec. III for the parameters of this state at this energy are also shown.

<table>
<thead>
<tr>
<th>Method</th>
<th>(\beta)</th>
<th>(\gamma)</th>
<th>(\epsilon)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Method A</td>
<td>2.5(5)</td>
<td>2.6(5)</td>
<td>1.2(5)</td>
</tr>
<tr>
<td>Method B</td>
<td>2.6(2)</td>
<td>2.7(2)</td>
<td>1.5(2)</td>
</tr>
<tr>
<td>Theory</td>
<td>2.51</td>
<td>2.81</td>
<td>2.00</td>
</tr>
</tbody>
</table>

Only method A allows the convenient generation of angular distribution parameter spectra as a function of energy.

For the rest of this paper we use signals obtained with \(\theta\) in the range \([0^\circ,90^\circ]\). As seen in Fig. 3 the measured angular distribution is not perfectly periodic with period 180\(^\circ\). This means that the angular distribution and parameters obtained with \(\theta\) in the range, e.g., \([90^\circ,180^\circ]\), will not be exactly the same. However, the fitted parameters derived from two different angle ranges differ by no more than 0.3, well within our ultimate error bar of 0.5.

Only four nonzero Legendre polynomial coefficients are allowed in Eq. (1b), as will be shown in Sec. III. However, due to noise and error in the experimental data, our measured \(d\sigma/d\Omega\) may have nonzero values for \(a_1, a_3, a_5, a_7, a_9\), etc. We found that when we fit our data to \(\sum a_nP_n(\cos\theta)\), where \(n=0,2,4,6,7,8\) and \(n=0,2,4,6,8,10\), we obtained essentially the same values for \(a_0, a_2, a_4, a_6\) as fitting the data to Eq. (1b). At the same time the values for \(a_7, a_8, a_9, a_{10}\), were consistent with zero. Including \(a_1, a_3, a_5\) in the fit caused a total loss of significance for all of the \(a_n\) values. Thus coefficients of order 7 or more were zero when included in the fit, and coefficients of order 1, 3, 5 are not defined when they are fit to our data, as expected.

III. THEORY

In order to derive specific formulas for the \(\beta\), \(\gamma\), and \(\epsilon\) parameters in Eq. (1a), we must start from the most general formula for \(d\sigma/d\Omega\) of an atom absorbing a linearly polarized photon and then emitting an electron:

\[
\frac{d\sigma}{d\Omega} = N^2 \sum_{J_x, J_z} \sum_{l,m,J,M_J} Y_{l,m}^* \langle \mathbf{k} \rangle \langle J'M'_J J_z M_z \rangle \langle J_z M_z l m \rangle \langle J z M z | M_J \rangle \langle \mathbf{k} - \mathbf{r} | J_0 \rangle^2 .
\]

This equation introduces most of the notation used in the rest of this paper. \(N^2\) is a normalization constant. \(J_z = J_x + s\), where \(s\) is the spin of the outer photolelectron; \(M_z\) is the projection of \(J_z\) on the axis defined by the laser polarization. \(l, m, l, m \rangle\) are the orbital angular momentum of the outer electron and its projection. \(J\) and \(M_J\) are the total angular momentum of the system, and its projection on the axis of quantization; \(J = J_x + I\). \(\mathbf{k}\) is the vector in the direction of the ejected electron's travel. The minus sign in the second matrix element indicates that the wave functions are normalized according to incoming-wave boundary conditions. \(\mathbf{\hat{e}}\) is the unit polarization vector of the last laser photon. The light is linearly polarized. \(r\) is the position of the Rydberg electron relative to the ion core. \(J_0\) and 0 are the initial total angular momentum of the Rydberg Mg atom before absorption of the third laser photon, and its projection on the axis of quantization. Due to the parallel linear polarization of our lasers, the 3nd states we use have \(J_0 = 2\), and the 3nd states have \(J = 1\) or 3.

Equation (2) can be expanded as

\[
\frac{d\sigma}{d\Omega} = N^2 \sum_{J_x, J_z} \sum_{l,m,J,M_J} Y_{l,m}^* \langle \mathbf{k} \rangle \langle J'M'_J J_z M_z \rangle \langle J_z M_z l m \rangle \langle J z M z | M_J \rangle \langle \mathbf{k} - \mathbf{r} | J_0 \rangle^2 \times \langle \{ J_0 \rangle | J_z M_z \rangle | J_M - | \mathbf{\hat{e}} \cdot \mathbf{r} | J_0 \rangle \rangle .
\]

Equation (3) can be written with reduced matrix elements as

\[
\frac{d\sigma}{d\Omega} = N^2 \sum_{J_x, J_z} \sum_{l,m,J,M_J} Y_{l,m}^* \langle \mathbf{k} \rangle \langle J'M'_J J_z M_z \rangle \langle J_z M_z l m \rangle \langle J z M z | M_J \rangle \langle \mathbf{k} - \mathbf{r} | J_0 \rangle^2 \times \langle J_0 | r(1) | J_x J_z l J_z - | \mathbf{\hat{e}} \cdot \mathbf{r} | J_0 \rangle \rangle .
\]

(4)

where \(r(1)\) is a first-rank tensor, and \([x]\) is defined as \((2x + 1)^{1/2}\). The portion of Eq. (4) in the large brackets, called \(A\), can be written as
\[
A = \begin{bmatrix} J_0 & 1 & J \\ 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} J' & 1 & J_0 \\ 0 & 0 & 0 \end{bmatrix} \sum_{m,M_{cs}} (-1)^m \sum_k \frac{[l][l']}{[k](4\pi)^{1/2}} \langle l'0l0|k0 \rangle \\
\times Y_{k0}(\hat{k}) \langle k0|l' - mlm \rangle \langle J'0|M_{cs}l'm \rangle \langle J_{cs}M_{cs}l'm|J0 \rangle,
\]

using the formulas for the product of \(Y_{lm}\) functions [26]. The \(Y_{k0}\) function can be written in terms of \(P_k(\cos \theta)\), giving

\[
A = -\frac{1}{4\pi} [J'][[l][l']] \begin{bmatrix} J_0 & 1 & J \\ 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} J' & 1 & J_0 \\ 0 & 0 & 0 \end{bmatrix} \sum_k [k]^2 P_k(\cos \theta) \begin{bmatrix} l' & l & k \\ 0 & 0 & 0 \end{bmatrix} \\
\times \sum_{m,m',M_{cs}} (-1)^m \begin{bmatrix} J_{cs} & l' & J' \\ M_{cs} & m' & 0 \end{bmatrix} \begin{bmatrix} J_{cs} & l & J \\ M_{cs} & m & 0 \end{bmatrix}.
\]

The portion of Eq. (6) in large brackets, called \(B\), is

\[
B = (-1)^{J_{cs}} \begin{bmatrix} k & J' & J \\ 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} k & J' & J \\ J_{cs} & l & l' \end{bmatrix}.
\]

By using the identity 6.2.8 of Ref. [27] the \(m\) dependences of the angular distribution are removed.

Combining Eqs. (3)–(7) we obtain

\[
\frac{d\sigma}{d\Omega} = \sum_k a_k P_k(\cos \theta),
\]

where

\[
a_k = \frac{-N^2}{4\pi} \sum_{J_{cs},J_{cs},l,l,l',J_{cs}} (-1)^l \langle [J'][[l][l']][k]^2 \begin{bmatrix} J_0 & 1 & J \\ 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} J' & 1 & J_0 \\ 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} l' & l & k \\ 0 & 0 & 0 \end{bmatrix} \\
\times \begin{bmatrix} k & J' & J \\ J_{cs} & l & l' \end{bmatrix} \begin{bmatrix} J_0 & \vec{r}^{(1)} \langle (J_{cs} J_{cs} l') J_{cs} \rangle J = \rho \langle (J_{cs} J_{cs} l') J' - \| \vec{r}^{(1)} \| J_0 \rangle.\]
\]

For the rest of this paper the reduced matrix elements in Eq. (8b) are abbreviated as \(D_{J_{cs}J_{cs}}^{\vec{r}}\) and \(D_{J_{cs}J_{cs}}^{l,l'}\), respectively. Only four terms in the summation of Eq. (8a) are nonzero due to the triangle rule for the \(3j\) symbols. The nonzero terms have \(k = 0,2,4,6\), confirming the form of Eqs. (1a) and (1b). Thus Eq. (8a) matches Eq. (1a), with \(J_{cs} = 4\pi a_0\), \(\beta = a_2/a_0\), \(\gamma = a_4/a_0\), and \(\epsilon = a_6/a_0\). Note that in calculating \(\beta\), \(\gamma\), and \(\epsilon\), the normalization \(N^2\) cancels out. For our particular final states, we can have \(J_{cs} = 0\) or 1, since \(J_{cs} = \frac{1}{2}\), \(s = \frac{1}{2}\), \(l = \frac{1}{2}\), and \(l' = J_{cs}\). When \(l = J = 1\) the ejected electron is an outgoing \(p\) wave. When \(l = J = 3\) the electron is an outgoing \(f\) wave. There are in general eight terms in the summation of Eq. (8b). Some of these terms are zero, depending on \(k\).

Evaluating Eq. (8a) with the aid of \(3j\) and \(6j\) tables, we calculate the angular distribution parameters in terms of the reduced matrix elements

\[
a_0 = \frac{\sqrt{3}}{15} ([D_{01}]^2 + [D_{11}]^2) + \frac{\sqrt{3}}{35} ([D_{03}]^2 + [D_{13}]^2),
\]

\[
a_2 = \frac{\sqrt{3}}{35} ([D_{01}]^2 - [D_{11}]^2) + \frac{\sqrt{3}}{15} ([D_{03}]^2 + 3[D_{13}]^2)
\]

\[
- \frac{\sqrt{3}}{35} [6 \text{ Re}(D_{01}^* D_{03}) + 2 \text{ Re}(D_{11}^* D_{13})],
\]

\[
a_4 = \frac{\sqrt{6}}{15} (6[D_{03}]^2 + [D_{13}]^2)
\]

\[
- \frac{\sqrt{6}}{15} [4\sqrt{6} \text{ Re}(D_{03}^* D_{03}) - 6 \text{ Re}(D_{13}^* D_{13})],
\]

\[
a_6 = \frac{\sqrt{6}}{15} (4[D_{03}]^2 - 3[D_{13}]^2),
\]

\[
\beta = a_2/a_0, \quad \gamma = a_4/a_0, \quad \epsilon = a_6/a_0.
\]

\[D_{J_{cs}J_{cs}}^{l,l'}\] is written out in Eq. (8b). Up to this point, our derivation is completely general, and we have not used MQDT.

Next we calculate the reduced matrix elements. This is where MQDT is essential. We have two manifolds of states, \(J = 1\) and \(J = 3\). For each manifold the derivations proceed in parallel; they are brought together only in Eq. (9). We use seven \(J = 1\) channels and eight \(J = 3\) channels. They can be described in \(J,J_{cs}\) or \(LS\) coupling. In
LS coupling the states are $3sep \, ^1P_1$, $3pns \, ^1P_1$, $3pnd \, ^1P_1$, $3sep \, ^3P_1$, $3pns \, ^3P_1$, $3pnd \, ^3P_1$, $3sep \, ^3D_1$, and $3pnd \, ^3D_3$, $3sef \, ^3F_3$, $3pnd \, ^3F_3$, $3pns \, ^3F_3$, $3sef \, ^3F_3$, $3pnd \, ^3F_3$, $3pns \, ^3F_3$, $3pg \, ^3G_3$. In $J_e, J_{cs}$ coupling the states $\phi_{J}$ are, for $J=1$, $3s_{1/2}\, |e\rangle$, $3s_{1/2}\, |n\rangle$, $3p_{1/2}\, |e\rangle$, $3p_{1/2}\, |n\rangle$, $3p_{3/2}\, |e\rangle$, $3p_{3/2}\, |n\rangle$, $3p_{1/2}\, |e\rangle$, and $3p_{1/2}\, |n\rangle$. For $J=3$ the states are $3s_{1/2}\, |e\rangle$, $3s_{1/2}\, |f\rangle$, $3s_{1/2}\, |e\rangle$, $3p_{1/2}\, |e\rangle$, $3p_{3/2}\, |n\rangle$, $3p_{3/2}\, |n\rangle$, $3p_{3/2}\, |n\rangle$, and $3p_{3/2}\, |n\rangle$. The number in braces is $J_{cs}$. Near the nucleus, LS coupling is the most physical due to the large electrostatic and exchange forces. At large distances the rate of phase accumulation depends on the energy of the core state, which in turn depends on $L_c$, $S_c$, and $J_c$. $L_c$ and $S_c$ are the total orbital angular momentum and spin of the core; $J_c = L_c + S_c$. At large distances $J_c, J_{cs}$ coupling is appropriate (actually $jj$ and $jK$ coupling [28] are as applicable as $J_c, J_{cs}$, but the matrix elements needed to describe the current angular distribution experiment are easier to evaluate in $J_c, J_{cs}$ coupling). The $K$ (reaction-reactance) matrix in $J_c, J_{cs}$ coupling can be obtained from the $K$ matrix in LS coupling through a simple transformation that represents the recoupling of the angular momenta and spins

$$K_{J_{cs}}^{J_c} = V_{J_{cs}}^{J_c} - K_{LS}^{J} V_{LS-1}^{J_c} ,$$

where

$$V_{J_{cs}}^{J_c} = \sum_{i,j} \phi_i^{J_c} (f_{ij} - g_{ij} K_{ij}) ,$$

when the outer electron is at distances larger than $r_0$. All wave functions $\psi$ are functions of the energy. $i$ and $j$ run over the states (channels) listed above. $f_{ij}(g_{ij})$ is the regular (irregular) Coulomb function of energy $e_i = E - E_j$ and angular momentum $l_i$. $E_i$ is the ionic core energy associated with the core of the $i$th channel, shown in Table

**TABLE II. $K^{J=1}$ Matrix.** The 7x7 matrix is evaluated at three different energies (relative to the Mg ground state). All matrix elements not included in the three block-diagonal submatrices shown here are zero.

<table>
<thead>
<tr>
<th>Energy (cm$^{-1}$)</th>
<th>$^1P$</th>
<th>$^3P$</th>
<th>$^3D$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3sep</td>
<td>3pns</td>
<td>3pnd</td>
</tr>
<tr>
<td>95 149</td>
<td>-1.29</td>
<td>2.71</td>
<td>0.860</td>
</tr>
<tr>
<td></td>
<td>2.71</td>
<td>-5.38</td>
<td>-1.77</td>
</tr>
<tr>
<td></td>
<td>0.860</td>
<td>-1.77</td>
<td>-0.823</td>
</tr>
<tr>
<td>97 344</td>
<td>-1.36</td>
<td>2.89</td>
<td>0.900</td>
</tr>
<tr>
<td></td>
<td>2.89</td>
<td>-5.87</td>
<td>-1.90</td>
</tr>
<tr>
<td></td>
<td>0.900</td>
<td>-1.90</td>
<td>-0.824</td>
</tr>
<tr>
<td>99 538</td>
<td>-1.38</td>
<td>3.00</td>
<td>0.910</td>
</tr>
<tr>
<td></td>
<td>3.00</td>
<td>-6.25</td>
<td>-1.98</td>
</tr>
<tr>
<td></td>
<td>0.910</td>
<td>-1.98</td>
<td>-0.807</td>
</tr>
</tbody>
</table>
TABLE III. $K^{J=3}$ matrix. The 8×8 matrix is evaluated at three different energies (relative to the Mg ground state). All matrix elements not included in the four block-diagonal submatrices shown here are zero.

<table>
<thead>
<tr>
<th>Energy (cm⁻¹)</th>
<th>$^3D$</th>
<th>$^3F$</th>
<th>$^3G$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3pnd</td>
<td>3s०f</td>
<td>3pnd</td>
</tr>
<tr>
<td>95 149</td>
<td>0.317</td>
<td>0.524</td>
<td>-0.0452</td>
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<tr>
<td></td>
<td>-0.0452</td>
<td>0.0116</td>
<td>-0.0608</td>
</tr>
<tr>
<td>97 344</td>
<td>0.306</td>
<td>0.552</td>
<td>-0.0400</td>
</tr>
<tr>
<td></td>
<td>-0.0400</td>
<td>0.0203</td>
<td>-0.0643</td>
</tr>
<tr>
<td>99 538</td>
<td>0.295</td>
<td>0.577</td>
<td>-0.0422</td>
</tr>
<tr>
<td></td>
<td>-0.0422</td>
<td>0.0260</td>
<td>-0.0640</td>
</tr>
</tbody>
</table>

IV. $E$ is the total energy of the excited state (above the Mg ground state). $K^{J=3}_{ij}$ is the $K$ matrix in $J_iJ_{cs}$ coupling. $^3A'$ is the antisymmetrization operator (which has no effect since the electrons are in different regions of space). $\psi_i^{J_i} = \chi_i^{J_i}$ are the $J_iJ_{cs}$ states. $\chi_i$ is the radial core function associated with the ionic core state. All of the $\psi_i^{J_i}$ states we consider have one of three possible core states: $3s_{1/2}$, $3p_{1/2}$, or $3p_{3/2}$.

The wave function of the 3snd "initial state" being photoionized can be written in a similar manner when the outer electron is at distances larger than $r_0$:

$$|J_0\rangle = \psi_{J_0}^{J_0} = ^3A\phi_{J_0}^{J_0}(|cos\mu_{JG} - sin\mu_{JG}|/\nu_0^{1/2},$$

where $\chi_0 = \chi_{3s}$, $L_c^0 = 0$, $S_{c}^0 = \frac{1}{2}$, $J_{cs}^0 = \frac{1}{2}$, $J_0^0 = 0$, $l_0 = 2$, $J_0 = 2$, and $\mu_0$ is the quantum defect of the initial state. $\nu_0$ is the effective quantum number of the 3snd state given by $\nu_0 = [R/(E_{3s} - E)]^{1/2}$. $R$ is the Rydberg constant for Mg: 109734.86 cm⁻¹. We have taken advantage of the fact that the initial-state LS coupling, 3snd $^3D$ is identical to the $J_iJ_{cs}$ coupling given here. In the isolated-core approximation the dipole operator only acts on the core electron due to the fact that the outer electron spends so little time near the nucleus that it cannot absorb a photon. Using this approximation the reduced dipole operator connecting MQDT wave functions (12) and (13) is

$$d_i^J = \langle \psi_i^J | r^{(1)} | \psi_{J_0}^{J_0} \rangle$$

$$= \sum_i \langle \phi_i^J | r^{(1)} | \phi_{J_0}^{J_0} \rangle$$

$$\times \int_{r_0}^{\infty} (cos\mu_{JG} - sin\mu_{JG}) f(r) \frac{dr}{v_0^{1/2}} .$$

Here again $i$ and $j$ run over the possible channels listed at the beginning of this section.

We derive an expression for $\langle \phi_i^J | r^{(1)} | \phi_{J_0}^{J_0} \rangle$ based on the repeated application of the formula for a tensor operator that only acts on a part of a coupled system (Eq. 7.1.7 of Ref. [27]). Due to the appearance of a zero in each of the resulting $6j$ coefficients, this expression reduces to a very simple formula

$$\langle \phi_i^J | r^{(1)} | \phi_{J_0}^{J_0} \rangle = \delta_l_{J_0}^{J_0} \delta_{J_{cs}}^{J_{cs}} \delta_{J_i}^{J_i} (|J_i| - 1) - 3/2 - J_i + J_0 + l_0$$

$$\times \int_0^{\infty} \chi_i(r) r d r / 3 \sqrt{2} .$$

In deriving Eq. (15) we used the fact that $L_c^0 = 0$, $J_{cs}^0 = 0$. Equation (15) applies to all isolated core experiments where the initial state is $m_{JG}J_{cs}$. We do not need to know the value of the dipole matrix element between $\chi_0$ and $\chi_i$ to obtain relative cross sections and angular distributions, since it is common to all of the nonzero terms.

Finally we obtain a value for the overlap of the outer electron's Coulomb functions by using Green's theorem:

$$\int_{r_0}^{\infty} (cos\mu_{JG} - sin\mu_{JG}) f(r) \frac{dr}{v_0^{1/2}} = 2\sqrt{2} v_0 v_f W(f_{G} cos\mu_{JG} - g_{G} sin\mu_{JG}, f_{JG} - g_{JG}, K_{JG}) / [v_0^{1/2}(v_i^2 - v_0^2)]$$

$$= 2\sqrt{2} \frac{v_f v_G}{v_0} (sin\mu_{JG} - cos\mu_{JG}) [\pi (v_i^2 - v_0^2)] ,$$

where $W(F,G) = F'G' - F'G'$ is the radial Wronskian evaluated at $r = r_0$, and $v_i = [R/(E_i - E)]^{1/2}$ is the effective quantum number in channel $i$. The last approximate step in Eq. (16) results from ignoring the energy dependence of the $f$ and $g$ at the small radius $r_0$, while using

$W(f,g) = 2/\pi$ and $W(f,f) = W(g,g) = 0$. Equation (16) contains the usual isolated-core approximations but is cast in a form more amenable to MQDT manipulations. We now combine the two pieces (15) and (16) into the full dipole matrix element to obtain
TABLE IV. Core energies of the Mg atom. Each energy given amounts to the energy necessary to remove one electron from the neutral atom and leave the Mg$^+$ core in the given state. $E_{3s}$ is simply the ionization energy of Mg. Energies are in cm$^{-1}$ above the ground state, with the neutral atom ground state defined to have zero energy.

\[
\begin{align*}
E_{3s} &= 61671.02 \\
E_{3p_{1/2}} &= 97340.33 \\
E_{3p_{3/2}} &= 97431.90
\end{align*}
\]

\[d_j^f = C(-1)^{l_0}[J] \times \sum_i \delta_{l_0,i} \delta_{l,i} \delta_{L_1} [L_j^f (-1)^{3/2-l_j^f} + l_0] \times \nu_1^2 (\sin \pi \mu_0 \delta_{ij} - \cos \pi \mu_k K_j^f) / (\nu_1^2 - \nu_3^2), \]  
\[\text{where } C \text{ is a factor common to all of the } d_j^f: \]
\[C = \sqrt{2} \nu_3 \int_0^\infty \chi_{3}\chi_{3}\chi_{3} d\chi / 3\pi.\]

We approximate $C$ to be the same whether it includes $\chi_{3p_{1/2}}$ or $\chi_{3p_{3/2}}$.

We construct the physical wave functions and dipole matrix elements by superposing the independent wave functions in Eq. (12) to eliminate exponentially diverging terms in the closed channels and satisfy normalization per unit energy in the open channels. The equations of these coefficients must satisfy the following conditions: When $j$ is a closed channel, $\epsilon_j = E - E_j < 0$, and

\[\sum_i (\tan \beta_j \delta_{ji} + K_j^i) A_{i\rho} = 0,\]  
\[\text{where } \beta_j = \pi(\nu_j - l_j). \text{ When } j \text{ is an open channel (i.e., } \epsilon_j > 0),\]

\[\sum_i \delta_{ji} A_{i\rho} = T_j^i \cos \pi \rho \]
\[\text{and}\]

\[\sum_i K_j^i A_{i\rho} = T_j^i \sin \pi \rho.\]

The $T_j^i$ matrix in Eqs. (19) is unitary. Since we have two open channels, $\rho$ runs from 1 to 2. Equations (19) can be combined in the usual way to obtain a generalized eigenvalue system where $\tan \pi \rho$ are the eigenvalues and $A_{i\rho}$ are the eigenvectors. The physical dipole matrix elements are obtained by superposition,

\[d_j^f = \sum_i d_j^f A_{i\rho},\]  
\[\text{or in a more conventional form, assuming only closed channels contribute,}\]

\[d_j^f = C(-1)^{l_0}[J] \sum_i \delta_{l_0,i} \delta_{l,i} \delta_{L_1} [L_j^f (-1)^{3/2-l_j^f} + l_0] \times \nu_1^2 \sin \pi (\nu_j - \nu_0) / (\nu_1^2 - \nu_3^2) \cos \pi \nu_1 A_{i\rho}.\]

The $d_j^f$ are real reduced dipole matrix elements that govern the transition from the ground state to the real wave function $\psi_j^f$. This standing wave does not satisfy boundary conditions corresponding to the experiment (with an electron escaping in a specific direction). This necessitates one further transformation to the solutions obeying the "incoming-wave boundary conditions," with outgoing waves only in channel $i$. The incoming-wave boundary condition is needed to represent a solution corresponding to photoelectron flux that escapes as a plane wave toward the detector only in channel $i$ at times $t \rightarrow \infty$. A clear discussion is given by Starace [29]. The final wave function is

\[\psi_j^f = \sum_{\rho} \psi_{\rho} T_{j\rho} \exp[i(l_j \pi/2 - \pi \rho \sigma_j - \sigma_j)],\]

where $\sigma_j$ is the Coulomb phase shift in channel $j$, $\sigma_j = \arg \Gamma(l_j + 1 - i/(2\epsilon_j)^{1/2})$, and $\epsilon_j$ is in atomic units. This final transformation achieves the goal of constructing a wave function that matches the experiment. We can now obtain the matrix elements needed for Eqs. (8b):

\[D_{j\rho}^f = \sum_{\rho} d_j^f T_{j\rho} \exp[i(l_j \pi/2 + \pi \rho \sigma_j + \sigma_j)].\]

The values of the $T_{j\rho}$ and $A_{i\rho}$ contained in $d_j^f$ are obtained by solving Eqs. (19). Equations (8) can now be used to generate cross sections and angular distributions.

To summarize, the sequence of transformations beginning with Eq. (10) is able to convert the dynamical information contained in nonrelativistic reaction matrices into photoionization cross sections and angular distributions obtained in isolated-core experiments. The necessary $K$ matrices are obtained from nonrelativistic $R$-matrix calculations. Since all of the other dynamical information is exact, the comparison of the current theory with experiment, described in Sec. IV, directly reflects on the precision of the $R$-matrix calculations.

IV. RESULTS AND DISCUSSION

A. Results

For each $3snd \rightarrow 3pnd$ transition, we have measured the ion signal yielding the total photoionization cross section. These line shapes have been measured and compared with theory in Ref. [3]. Our measured line shapes agree with those in Ref. [3], and they agree quite well with theory, as shown in Ref. [3].

Our measurements of the angular distribution parameters $\beta$, $\gamma$, and $\epsilon$ are shown in Figs. 4, 5, and 6. The superimposed smooth solid lines are the MQDT predictions for the parameters. Figure 4 shows the parameters for the $3s10d \rightarrow 3p10d$ transition, over a range of cm$^{-1}$ centered on the peaks of the transition. Figure 5 shows the $3s12d \rightarrow 3p12d$ transition over the same energy range as Fig. 4. Figure 6 shows the $3s18d \rightarrow 3p18d$ transition over a narrower energy range to better exhibit the narrower features of the higher $n$ spectra. In each graph, the parameters have the same vertical scale but are offset vertically for the sake of clarity. In each case the theoretical prediction was convolved with the 1 cm$^{-1}$ instrumental linewidth of our measurements, reducing the sharpness of some of the narrow features, especially in
FIG. 4. Angular distribution parameters $\beta$, $\gamma$, and $\epsilon$ for the $3s10d \rightarrow 3p10d$ transition. The experimental results are shown with the jagged solid line. The error of our derived values for $\beta$, $\gamma$, and $\epsilon$ vary across the graph, however, a typical $1\sigma$ error for the parameters is 0.5. The predictions of the $K$ matrix-MQDT theory as described in the main text are shown with a smooth solid line. The results of the alternate MQDT theory formulation using earlier $K$ matrices of Refs. [2,3], described in the Appendix, are shown as a dotted line. Each horizontal line indicates the zero for the corresponding parameter that overlaps it. $\sigma_j$ is the relative photoionization cross section (in arbitrary units) contributed by the $J=1$ (solid curve) and $J=3$ (dash-dotted curve) final states. The narrowest peak heights have been artificially chopped off. Unlike the parameters $\beta$, $\gamma$, and $\epsilon$, the cross section has not been convoluted with the experimental resolution ($1 \text{ cm}^{-1}$). The top of the figure shows the effective quantum number scales going to the two $3p_{1/2}$ and $3p_{3/2}$ fine-structure thresholds in unit steps.

FIG. 5. Angular distribution parameters $\beta$, $\gamma$, and $\epsilon$ for the $3s12d \rightarrow 3p12d$ transition. The comments of Fig. 4 apply to this graph.
the $n = 18$ parameters. The positions of the unperturbed Mg$^+$ ion transitions $3s_{1/2} \rightarrow 3p_{1/2}$ and $3p_{3/2}$ are at positions 35 669 cm$^{-1}$ and 35 761 cm$^{-1}$, respectively. Although we measured the angular distribution parameters for all of the $3pnd$ states with $n = 10–18$, we show only three sets of parameters. All differ in detail, but exhibit similar qualitative features and shapes. For $n \geq 19$, the features of the spectra became quite narrow, and our laser linewidth was a limiting factor.

The errors in our values for $\beta$, $\gamma$, and $\epsilon$ come from several sources, listed below in order from largest to smallest. The two largest sources of error are random in nature, and are due to the random fluctuations (noise) in the signal levels, when all of the lasers are fixed in frequency and the signal should remain constant. The largest error comes from the self-consistency, or repeatability, of our results for the angular distribution parameters. We checked this by going through the data analysis procedure of Sec. II using different sets of electron signals at certain angles, all corresponding to the same transition. That is, instead of using all of the measured electron signals at, e.g., $\theta = 0^\circ, 21^\circ, 31^\circ, 34^\circ, 49^\circ, 55^\circ, 62^\circ, 70^\circ, 76^\circ, 90^\circ$, we used just four electron spectra at $\theta = 0^\circ, 31^\circ, 55^\circ, 90^\circ$ and fit Eq. (1b) to them. (The angles were chosen to be extremes or roots of the various Legendre polynomials, and to be distributed as evenly as possible over the range 0–90$^\circ$.) We did this for several different sets of four out of ten angles. The angular distribution parameter spectra obtained agreed with each other to within approximately 0.3 or less at the peaks of the line shapes. (The numbers for the angular distribution parameters have no units.)

The other random error due to noise in the signals appeared as the fitting error. In essence this error reveals the consistency of our data with Eq. (1b). The standard deviations of $\beta$, $\gamma$, and $\epsilon$ due to the fitting error were obtained via Gaussian error propagation from the fitting errors for the parameters $a_0, a_2, a_4, a_6$. The $a_k$ fitting errors were the square roots of the diagonal elements of the covariance matrix returned by the fitting algorithm [25]. These fitting errors represent the minimum error possible. These errors depend on the estimate of error of our electron signal to ion signal quotients; the quotient error was obtained via Gaussian error propagation from the Poisson errors of the electron and ion signals. The quotient errors were in the range [0.01, 0.15]. The fitted values of $\beta$, $\gamma$, and $\epsilon$ were insensitive to these input error values. The fitting errors of $\beta$, $\gamma$, and $\epsilon$ were very small at energies corresponding to peaks of the line shapes, but grew to about 1.0 at energies where the electron and ion signal values were very small. This indicated that at small electron signal values, where $d\sigma/d\Omega$ and $I_\theta$ were nearly zero, the parameters $\beta$, $\gamma$, and $\epsilon$ were not well defined, due to the form of Eq. (1a).

The rest of the errors, smaller in magnitude than the two previously described, were systematic in nature. It is possible that the angle $\theta$ at which we set the laser polarization was in fact $\theta + \delta$. $\delta$ would have been the same for all $\theta$. This systematic offset of $\theta$ could be caused, for example, by a tilt of the linear polarizers relative to the vacuum chamber and detectors. The fitting algorithm, using the misrepresented values of $\theta$ for the electron signals, would then return incorrect values for $\beta$, $\gamma$, and $\epsilon$. We estimate $\delta$ for our apparatus is less than 2$^\circ$. We simulated this effect of nonzero $\delta$ by generating on a computer electron signals at various $\theta$ from a given angular distribution described by $\beta$, $\gamma$, and $\epsilon$. The angles $\theta$ were altered to be
\( \theta + \delta \), and the electron signals labeled by their altered angles were then treated as real data and fit to Eq. (1), generating new \( \beta', \gamma', \) and \( \epsilon' \). For \( |\delta| \leq 2^\circ \) the original and transformed angular distribution parameters agreed to within approximately 0.2 or less. For \( |\delta| \geq 5^\circ \) the transformed parameters \( \beta', \gamma', \) and \( \epsilon' \) were drastically changed from their original values, so accurate angular alignment was critical.

Another systematic error could be caused by a nonzero offset to the dc signal level outputs of the gated integrators. As described earlier, we carefully set the offset to be no more than a tenth of the signal for each scan. Artificially shifting the dc offset of some or all of the electron signals in a set by 1 part in 10 had no noticeable effect on the parameters. The ion signals in general were larger than the electron signals, and their zero offset was always a small fraction of their signal value over the energy ranges examined.

A final possible systematic error is due to the nonzero solid angle of our detector. The finite size of the detector caused it to convolve or average the angular distribution over its 0.2 radian width. We simulated this effect by calculating the angular distribution at each energy from theoretically generated parameter spectra and averaging it over a 0.2 radian width. Then we treated that averaged angular distribution as real data and fit Eq. (1) to it. Repeating this procedure at each energy generated new parameter spectra. At a detector width of 0.2 radians, the \( \beta \) and \( \gamma \) spectra did not change at all. The \( \epsilon \) parameter, since it multiplies \( P_\epsilon(\cos \theta) \), varies the most rapidly with \( \theta \), would be expected to be the most sensitive to this effect. At a width of 0.2 radians, the absolute value of \( \epsilon \) decreased significantly in a few places, by no more than 0.05 from the original \( \epsilon \) spectra.

Taking all of these error sources together, the total error (one standard deviation) in the \( \beta, \gamma, \) and \( \epsilon \) angular distribution parameters is at most 0.5, including both random and systematic errors. Thus the error bars on our parameter values vary, but have a typical half width of 0.5. Near the peaks of the line shapes the repeatability of our \( \beta, \gamma, \) and \( \epsilon \) parameter values (excluding systematic errors) was 0.2 or better. Due to the more complex data-taking and analysis procedures, these errors are significantly larger than the error on the \( \beta \) parameter of the 3pns Mg states [19]. The energy resolution of our spectra, determined by our laser linewidth, was about 1.0 cm\(^{-1}\).

**B. Discussion**

In the previous work on the 3pns Mg angular distribution parameter [19], the \( \beta \) parameter was found to be relatively constant near \( \beta \approx -1 \), except for a few sharp dips to \( \beta \approx 1 \). That sort of structure is not seen in these 3pnd angular distribution spectra. Instead we measured parameter values, which vary irregularly. The fluctuations of the \( \beta \) parameter of the 3pns states were clearly correlated with the positions of interloping autoionizing states, which were not excited directly, but were at the same energies as the \( \beta \) parameter fluctuations. Although there are similar interloping resonances throughout the measured energy range of the 3pnd states, there is no obvious correlation between them and the features in the 3pnd angular distribution spectra. The 3pnd spectra are considerably more complex than the 3pns spectra, which is to be expected since the 3pnd states studied are more complex and have two angular momentum \( J \) manifolds.

As shown by Figs. 4, 5, and 6 the predicted \( \beta, \gamma, \) and \( \epsilon \) spectra agree well with our measurements. Most of the small disagreement between experiment and theory can be explained by experimental error. The only significant systematic discrepancy is that the measured \( \epsilon \) value is never more than about 2, whereas the theoretical value of \( \epsilon \) reaches 3 at some energies. Since \( \epsilon \) multiplies \( P_\epsilon(\cos \theta) \), which varies most rapidly with \( \theta \), the \( \epsilon \) parameter is most sensitive to systematic offsets in \( \theta \), and to the averaging of the angular distribution over \( \theta \). It is possible that we have underestimated the averaging of the angular distributions caused by the finite angular aperture of our electron detector. This would cause us to measure a smaller \( |\epsilon| \) than the true \( |\epsilon| \), but would have little effect on \( \beta \) and \( \gamma \).

The different sorts of angular distributions observed are shown as polar plots in Fig. 7, along with the angular distribution of the 3snd \( ^1D \) level being photoionized. The expected propensity is that the photoelectron will be mainly ejected along the photon polarization axis. This is because the 3snd level is already elongated in that direction, and also because the photoionizing laser is applying an additional force on the electron cloud in that direction. If a low-lying 3snd level was being photoionized rather than a Rydberg level, one would argue [30,31] that the nd electron would be preferentially photoionized into the ef continuum rather than into the ep continuum. The classical argument is that in the course of absorbing energy and increasing in speed, the photoelectron is more likely to gain rather than lose angular momentum (a quantum version of this argument is given in Ref. [30]).

This simple argument needs to be modified to understand the present experiment, because it is really the 3s electron that is initially excited by the photoionizing laser, after which the 3pnd resonance levels decay by autoionization into the 3sep and 3sef continua. But a similar argument still applies in that the nd electron gains speed in the course of autoionizing and so has a propensity to gain angular momentum. For this reason the 3pnd \( \rightarrow \) 3sef channel should be the dominant photoionization pathway. This propensity is verified by the relative \( J = 1 \) and 3 contributions to the total photoionization cross section, shown in Figs. 4—6. The \( J = 3 \) line shapes are much broader on average than \( J = 1 \) line shapes since there is more of a propensity to autoionize to an f-wave continuum (the autoionization rate to f waves is faster). Therefore over most of the spectra, except near high and narrow \( J = 1 \) resonances, the \( J = 3 \) contribution is larger than the \( J = 1 \) contribution.

Because a pure f-wave solution with \( m_f = 0 \) is highly peaked along the quantization axis, this confirms that ejection along the polarization axis should be greatly favored (normally) over sideways photoejection near \( \theta = \pi/2 \). This propensity is verified in the angular distributions of the present experiment, with most energies
FIG. 7. (a) Angular distribution of the initial $|J_{ee}\rangle$ $3s3d$ state. $|\Psi|^2$ is proportional to $[P_r |\cos\theta|]^2$. (b) A typical “propensity favored” angular distribution. This is of the $3p18d$ state at 35 646 cm$^{-1}$ above the $3s18d$ state. The solid line is the MQDT prediction for the angular distribution [of the form of Eq. (1a)]. The filled circles are the measurements of the normalized electron signal (differential cross section) $\Psi=0$ vertical on these polar plots. We measured $d\sigma/d\Omega$ only in the plane of the paper, and only on the interval [0°, 90°]. The data have been copied onto the other three quadrants. The dashed line is a least-squares fit of the data to Eq. (1a). The parameters $\beta$, $\gamma$, and $\epsilon$ derived from the fit are the three data points of Fig. 6 at 35 646 cm$^{-1}$. The peak of $d\sigma/d\Omega$ along the quantization (laser polarization) axis is typical of photoionization. (c) A “propensity unfavored” angular distribution. This is of the $3p18d$ state at 35 687 cm$^{-1}$ above the $3s18d$ state. This graph shows that at a few particular energies the electron can be ejected “sideways” due to the complex channel interactions.

displaying a photoelectron angular distribution peaked along the polarization vector, qualitatively similar to that shown in Fig. 7(b). Occasionally energies are probed, as in Fig. 7(c), which shows the propensity-unfavored case of predominantly sideways photoejection, but these tend to be comparatively rare.

A further complication to bear in mind when comparing the present theory and experiment is that the calculation has ignored all effects of hyperfine structure. For 90% of the Mg atoms, which have zero nuclear spin, this is exact. But for the remaining 10% having nuclear spin $I=\frac{5}{2}$, the hyperfine interaction causes $J$ to precess about $F$, which can mix in the magnetic substates other than $M_J=0$. The validity of ignoring this precession depends on the relative time scales of hyperfine precession and of the laser excitation time. The precession periods are estimated to fall in the range of 10 to 25 ns for the Mg $3s3p^1P^0$ state, which is slow though not entirely negligible compared to the 5 ns delay between absorption of the first and second laser photons. Since this affects only 10% of the atoms, however, this is likely to cause less than a 1–2% correction to the anisotropy parameters calculated in this study. The hyperfine precession appears to be negligible for singlet Rydberg states in the range studied here.

Equations (9a)–(9e), which form the angular distribution parameters, can be rewritten in terms of probabilities $P_{J_{ee}J}$, where $P_{J_{ee}J}$ represents the fraction of the total photoionization cross section contributed by states with $J_{ee}$ and $J$. If $P_{J_{ee}J}$ is written as the square of a complex probability amplitude $|A_{J_{ee}J}|^2=|P_{J_{ee}J}$, then the $A_{J_{ee}J}$ are proportional to the $D_{J_{ee}J}$ of Eqs. (9). For example, $A_{01}=(i\frac{\beta}{13})^{1/2}P_{01}/(a_0)^{1/2}$, etc. Then Eqs. (9b)–(9e) can be rewritten as

$$\beta=2P_{01} - P_{11} + \frac{4}{3}P_{03} + P_{13} - 6(\frac{3}{5})^{1/2}\text{Re}(A_{01}^*A_{03})$$

$$- 6(\frac{3}{5})^{1/2}\text{Re}(A_{11}^*A_{13})$$

$$\gamma=\frac{18}{11}P_{03} + \frac{1}{11}P_{13} - 8(\frac{3}{5})^{1/2}\text{Re}(A_{01}^*A_{03})$$

$$+ 6(\frac{3}{5})^{1/2}\text{Re}(A_{11}^*A_{13})$$

$$\epsilon=\frac{100}{33}P_{03} - \frac{23}{33}P_{13}$$

The $P$s must be in the range [0,1], and the $A$'s must have a magnitude less than or equal to 1. Also the sum $P_{01} + P_{11} + P_{03} + P_{13}$ must equal 1 for all cases. These constraints allow one to determine the maximum and minimum values of the parameters. $\epsilon$ clearly lies in the range $[-2.27,3.03]$. A Monte Carlo calculation using all possible values of the $A$'s shows that $\beta$ is in the range $[-1.86,3.65]$, and $\gamma$ is in the range $[-1.92,3.56]$. These limits agree very well with our measurements, and agree perfectly with our theoretical results. The excursions of our measured parameters past these limiting values are due to noise in the data.

In order to understand the forms of the $\beta$, $\gamma$, and $\epsilon$ parameter spectra, we shall discuss the contributions to the
theoretical parameter spectra. As shown by Eq. (9) the terms that form \( \beta, \gamma, \) and \( \epsilon \) can be divided into three categories. The pure \( J = 1 \) terms contain only matrix elements of the form \( |D_{\epsilon|a}|^2 \). The pure \( J = 3 \) terms contain only elements of the form \( |D_{a|a}|^2 \). The “mixed \( J \)” terms are of the form \( \text{Re}(D_{\epsilon|a}^*D_{\epsilon|a}) \). The \( a_0 \) parameter contains pure \( J = 1 \) and \( 3 \) terms but no mixed \( J \) terms. \( a_2 \) contains all three types of terms. \( a_4 \) contains no pure \( J = 1 \) terms, and \( a_6 \) contains only pure \( J = 3 \) terms. Thus \( \beta \) and \( \gamma \) contain mixed \( J \) terms, while \( \epsilon \) does not. This is since in the calculation of \( a_4 \), as \( k \) increases, more and more of the terms in the summation of Eq. (8b) are zero, due to the triangle rule for the \( 3j \) symbol \( ^{3j}_{00} \), with \( J \) and \( J' \) never more than 3.

We can separate the contributions of the three categories of matrix element products to the theoretical \( \beta \) spectrum of the 3p12d state, as shown in Fig. 8. The top line of Fig. 8 shows the pure \( J = 1 \) contributions to \( \beta \). In other words, the top line is a graph of

\[
\frac{\frac{1}{15}(2|D_{00}|^2 - |D_{11}|^2)}{a_0}
\]

The line labeled \( J = 3 \) shows the pure \( J = 3 \) contribution to \( \beta \); it is a graph of

\[
\frac{\frac{1}{35}(4|D_{00}|^2 + 3|D_{11}|^2)}{a_0}
\]

The line labeled mixed \( J \) is a graph of

\[
\frac{\frac{1}{35}(\sqrt{6} \text{Re}(D_{00}^*D_{00}) + 2 \text{Re}(D_{11}^*D_{11}))}{a_0}
\]

the mixed \( J \) contribution to \( \beta \). In each case the full \( a_0 \) of Eq. (9a) is used, so that the sum of the three partial \( \beta \) parameters is the total \( \beta \). This means the \( J = 3 \) line, for example, still has some \( J = 1 \) contribution coming from \( a_0 \) in the denominator.

Figure 9 shows the same arrangement for the theoretical \( \gamma \) parameter of the 3p12d state. Since \( a_4 \) has no pure \( J = 1 \) terms, the top line of Fig. 8 is missing from Fig. 9 (\( \epsilon \) has only pure \( J = 3 \) terms, so it cannot be divided up in the same way as \( \beta \) and \( \gamma \).

Figures 8 and 9 show clearly that the structure of the \( \beta \) and \( \gamma \) parameters is overwhelmingly due to the mixed \( J \) terms of the \( a_2 \) and \( a_4 \) parameters. The shapes of the total \( \beta \) and total \( \gamma \) graphs are quite similar to the mixed \( J \) term graphs. The pure \( J = 1 \) and \( J = 3 \) term graphs tend to fluctuate as a function of energy much less than do the

Fig. 8. Various contributions to the \( \beta \) parameter spectrum of the 3p12d state of Mg. In order from top to bottom, the graphs are of the \( \beta = a_2/a_0 \) parameter with \( a_2 \) consisting only of pure \( J = 1 \) terms, only of pure \( J = 3 \) terms, and only of mixed \( J \) terms. In all cases the \( a_0 \) used is the full \( a_0 \) of Eq. (9a). The bottom line is the complete \( \beta \) parameter, which is the sum of the top three graphs. This figure is purely theoretical. As in Figs. 4–6 the solid horizontal lines indicate the zeros of the parameters. As discussed in the text the mixed \( J \) terms provide the major contribution to the total \( \beta \) parameter shape.

Fig. 9. Similar to Fig. 8, this figure shows the various contributions to the \( \gamma \) parameter spectrum of the 3p12d state of Mg. In order from top to bottom, the graphs are of the \( \gamma = a_4/a_0 \) parameter with \( a_4 \) consisting only of pure \( J = 3 \) terms, then only of mixed \( J \) terms, and on the bottom the sum of the top two, which is the total \( \gamma \) parameter. The \( a_0 \) used is the full \( a_0 \) of Eq. (9a). The \( \gamma \) parameter has no pure \( J = 1 \) terms. As with the \( \beta \) parameter, the mixed \( J \) terms provide the major contribution to the total \( \gamma \) parameter shape.
mixed $J$ term graphs and so they contribute less to the shape of the total $\beta$ and $\gamma$ parameters. The pure $J=1$ and 3 terms do contribute significantly to the numerical values of the $\beta$ and $\gamma$ parameters.

In Figs. 4–6 there appears to be a pattern of sharp shifts, peaks, or dips near the peaks of the line shape. The peaks of the transition line shapes are mostly due to very narrow $J=1$ features in the spectra. As shown in the total-cross-section traces in Figs. 4–6 and in Ref. [3], the line-shape signal due to $J=1$ 3pnd states has only very narrow and high peaks, with almost no signal between the peaks. The $J=3$ 3pnd line shape is more slowly varying with energy and has broad peaks that overlap each other. An angular distribution can be derived from the $J=1$ states only and from the $J=3$ states only; each is different. Over most of the energy range the $J=3$ line shape predominates; so the total angular distribution parameters mostly reflect the $J=3$ distribution. Only at the narrow peaks of the line shape would the separate $J=1$ distribution predominate; there, the total angular distribution would reflect the $J=1$ distribution. The $\epsilon$ parameter shows the clearest distinction between $J=1$ and $J=3$ contributions. The $\epsilon$ parameter has a $J=1$ contribution only via the $a_0$ denominator. A pure $J=3$ $\epsilon$ parameter can be written by eliminating the $J=1$ portion of $a_0$. This altered $\epsilon$ is given as

$$
\epsilon' = \frac{4(4|D_{12}|^2 - 3|D_{13}|^2)}{\frac{1}{2}|D_{12}|^2 + |D_{13}|^2}.
$$

$\epsilon'_{J=3}$ has a graph similar to the unaltered $\epsilon$, as shown in Fig. 10, however $\epsilon'_{J=3}$ has no sharp dips interspersed among the broad fluctuations. These sharp dips, and the other features of the parameters that vary rapidly with energy, are due to the $J=1$ contributions. Examples of these $J=1$ features are the parameters of 3p12d at 35 690 and 35 860 cm$^{-1}$, and of 3p10d at 35 635 cm$^{-1}$.

Relatively weak and narrow features due to $g$ states can be seen in the measured and theoretical spectra, e.g., in the 3p12d angular distribution of Fig. 5 at 35 668 cm$^{-1}$. These must be due to $J=3$ 3png states since the features do not appear in the theoretical calculations which exclude $g$ states, shown as dotted lines in Figs. 4–6.

V. CONCLUSION

We have measured the angular distributions of autoionizing electrons ejected from 3pnd $J=1$ and $J=3$ states of Mg and have obtained their angular distribution parameter spectra over the range of $n$ from 10 to 18. The measured spectra are complex and irregular. They appear drastically different from the 3pns $J=1$ angular distribution parameter spectra measured previously [19]. We have also calculated the angular distribution parameter spectra using $K$ matrices and an MQDT formalism. The calculated 3pnd spectra agree well with the measured 3pnd spectra, to within experimental error.

We find that the different $J$ states can produce interference in the emitted electron spectra, but only in some ($\beta$ and $\gamma$) angular distribution parameter spectra. In the $\epsilon$ parameter spectra and in the total cross section $\sigma$, the different $J$ states do not interfere.

The line-shape measurements of Mg autoionizing states reported in Refs. [2] and [3], the angular distribution measurements in Ref. [19] of the Mg 3pns $J=1$ states, and the angular distribution measurements of the Mg 3pnd $J=1$ and 3 states described in this paper form a progression of measurements that involve successively more and more complex sets of channels and wave functions. The quantities measured represent successively more and more stringent tests of the $K$ matrices and of the $R$-matrix approach itself. The less stringent test described in Refs. [2] and [3] results in quite good agreement between theory and experiment. The test of intermediate stringency, involving the angular distribution of the relatively simple 3pns $J=1$ states excited by one photon from a spherically symmetric $J=0$ state, shows good agreement, but there are a few significant discrepancies [19]. This paper measures the angular distributions of the fairly complex 3pnd states with relatively high angular momentum, and for these states the $K$ matrices also match well with the measurements.

ACKNOWLEDGMENT

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APPENDIX

This appendix contains an alternate means of calculating the reduced matrix elements $D_{1,j}$ of Eq. (22). This formulation can replace Eqs. (10)–(22), and was derived independently. As can be seen in Figs. 4–6, the results of each formulation are essentially the same, serving as a check on the validity of both.

The final dissociation states, in which the electrons are far apart, are most naturally described by $jj$ coupling, so in this formulation we work in the $jj$ coupled scheme, converting the $K$ matrix to $jj$ coupling. (In all of the fol-
The orthogonal matrices \( V^1 \) and \( V^3 \) are given in Refs. [19] and [2], respectively. For this alternate derivation of the \( D_{J\rho} \) we use the older \( K \) matrices of Ref. [2] (\( J = 1 \)) and Ref. [3] (\( J = 3 \)). These were calculated with a box size of \( r_0 = 12 \) a.u. and do not include 3p3n states. As described in detail in Ref. [19], those \( K \) matrices allow us to calculate the channel amplitudes \( A_{J\rho} \), where

\[
\Psi_\rho = \sum_i A_{J\rho}^i \phi_i^J .
\]

(\( A3 \))

\( \Psi_\rho \) is the collision eigenstate of the system after ionization. For each \( J \) there are two open channels, and so two collision eigenstates that are labeled by \( \rho = 1, 2 \). The \( \Psi_\rho \) are linear combinations of the \( jj \) coupled channels. Via the procedures described in detail in Ref. [19] we also obtain the phase shifts \( \gamma_{J\rho}^a \) of the open-channel continuum wave functions from the \( K \) matrices.

Since our reduced matrix element kets \([J, s | J_\alpha \kappa | J] \) are in \( J, J_\alpha \) coupling, which in this case is equivalent to \( LS \) coupling, since for our final states \( J_\alpha = S \) and \( l = L \), we must also convert them to \( jj \) coupling before using them. This can be done using submatrices of the \( V^J \)'s of Eqs. (A1) and (A2). In particular, we will need

\[
\begin{align*}
\langle [J_\alpha = 0 l = 1 | J = 1 ] & \rangle = 3s e p^1 p_1 \quad W_{11}^1 \quad W_{12}^1 \quad \phi_1^J \\
\langle [J_\alpha = 1 l = 1 | J = 1 ] & \rangle = 3s e p^3 p_1 \quad W_{21}^1 \quad W_{22}^1 \quad \phi_2^J \\
\langle [J_\alpha = 0 l = 3 | J = 3 ] & \rangle = 3s e f^1 f_3 \quad W_{11}^3 \quad W_{12}^3 \quad \phi_1^J \\
\langle [J_\alpha = 1 l = 3 | J = 3 ] & \rangle = 3s e f^3 f_3 \quad W_{21}^3 \quad W_{22}^3 \quad \phi_2^J \end{align*}
\]

(A4)

and

\[
\begin{align*}
\langle [J_\alpha = 0 l = 3 | J = 3 ] & \rangle = 3s e f^1 f_3 \quad W_{11}^3 \quad W_{12}^3 \quad \phi_1^J \\
\langle [J_\alpha = 1 l = 3 | J = 3 ] & \rangle = 3s e f^3 f_3 \quad W_{21}^3 \quad W_{22}^3 \quad \phi_2^J \\
\langle [J_\alpha = 0 l = 1 | J = 1 ] & \rangle = 3s e p^1 p_1 \quad W_{11}^1 \quad W_{12}^1 \quad \phi_1^J \\
\langle [J_\alpha = 1 l = 1 | J = 1 ] & \rangle = 3s e p^3 p_1 \quad W_{21}^1 \quad W_{22}^1 \quad \phi_2^J \end{align*}
\]

(A5)

The \( W^J \) matrices are simply subblocks of the \( V^J \) matrices corresponding to the open channels.

We may now write the reduced matrix elements \( D_{J_\alpha, J} \) as

\[
D_{01} = \langle [J, s | J_\alpha = 0 l | J = 1 ] | r^{(1)} | J_0 \rangle = \sum_{i=1}^{2} W_{i1}^1 \langle \phi_i^J - | r^{(1)} | J_0 \rangle \\
= \sum_{i=1}^{2} W_{i1}^1 \sum_{\rho=1}^{2} \langle \phi_i^J | \Psi_\rho \rangle \langle \Psi_\rho - | r^{(1)} | J_0 \rangle \\
= \sum_{i=1}^{2} \sum_{\rho=1}^{2} W_{i1}^1 \sum_{j=1}^{7} \langle \phi_i^J | \phi_j^J \rangle A_{j\rho}^J \sum_{k=1}^{7} A_{k\rho}^J \langle \phi_k^J - | r^{(1)} | J_0 \rangle \\
= \sum_{i=1}^{2} \sum_{\rho=1}^{2} W_{i1}^1 A_{i\rho}^J \sum_{k=5}^{7} A_{k\rho}^J \langle \phi_k^J - | r^{(1)} | J_0 \rangle \\
= \sum_{i=1}^{2} \sum_{\rho=1}^{2} \sum_{k=5}^{7} W_{i1}^1 A_{i\rho}^J A_{k\rho}^J M_{k\rho}^J .
\]

(A6a)
using \( \sum \left| \Psi_j \right> \left< \Psi_j \right| \) and \( \left| J_0 \right> = \left| 3snd \right> D_2 \). Here
\[
M_{k_p} = \left< \phi_{k}^j \left| r \right| \left| J_0 \right> \right>. \tag{A6b}
\]
\[
D_{11} = \sum_{i=1}^{2} \sum_{\rho=1}^{2} \sum_{k=1}^{7} W_{i}^{11} A_{i\rho}^{11} A_{k\rho}^{11} M_{k_p} \tag{A6c}
\]
\[
D_{03} = \sum_{i=1}^{2} \sum_{\rho=1}^{2} \sum_{k=1}^{5} W_{i}^{03} A_{i\rho}^{03} A_{k\rho}^{03} M_{k_p} \tag{A6d}
\]
\[
D_{13} = \sum_{i=1}^{2} \sum_{\rho=1}^{2} \sum_{k=1}^{3} W_{i}^{13} A_{i\rho}^{13} A_{k\rho}^{13} M_{k_p} \tag{A6e}
\]

Reading from right to left, the factors in the last form of Eq. (A6) can be understood as follows: \( M_{k_p} \) is the dipole matrix element connecting the bound initial \( 3snd \) state to the \( k \)th closed channel. \( A_{i\rho}^{11} \) is the amplitude of the \( i \)th channel in the right eigenchannel. Summing \( A_{i\rho}^{11} M_{k_p} \) over \( k \) gives the amplitude for excitation of the \( \rho \)th eigenchannel. \( A_{i\rho}^{03} \) is the amplitude of the \( i \)th open channel in the \( \rho \)th eigenchannel, and is thus the fractional amplitude for decay into the \( \rho \)th open channel. Finally \( W_{i}^{13} \) gives the fraction of the \( i \)th channel that is singlet, and \( W_{i}^{03} \) gives the fraction that is triplet. When all the factors are put together the \( D_{m_p} \) matrix element is the amplitude for the transition from the initial \( 3snd \) state to the \( J_p, J \) continuum.

The states \( \left| \phi_j^p \right> \) listed in Eqs. (A1) and (A2), with \( j = 5, 6, 7 \), for \( J = 1 \) and \( k = 3, 4, 5 \) for \( J = 3 \) will be written now as \( \left| 3p_j, \nu \right> \), where \( \nu \) is the effective principal quantum number of the outer electron's state. \( \nu \) is not necessarily an integer. \( \nu \) is determined by the ionization potential \( E_{j'} \) with respect to the excited ion core. \( J'_p \) is the total angular momentum of the excited ion core. \( \nu \) of a state with \( J'_p \) is given by
\[
\nu = \left[ \frac{R}{E_{j'}} - E \right]^{1/2}, \tag{A7a}
\]
where \( R \) is the Rydberg constant for Mg: 109734.86 cm\(^{-1} \). \( E \) in Eq. (A7a) is the total energy of the autoionizing state. \( E_{3p_{1/2}} \) is 97340.33 cm\(^{-1} \) and \( E_{3p_{3/2}} \) is 97431.90 cm\(^{-1} \). When rewriting the initial state \( \left| J_0 \right> \),
\[
\nu = \left[ \frac{R}{E_{3s} - E} \right]^{1/2}, \tag{A7b}
\]
where \( E_{3s} \) is the normal ionization potential of Mg with an unexcited core 61671.02 cm\(^{-1} \) and \( E \) in Eq. (A7b) is

the energy of the \( \left| J_0 \right> \) state [22]. Note that \( \left| J_0 \right> \) in \( jj \) coupling is \( \left( \frac{1}{2} \right)^{1/2} \left| 3s_{1/2} \right> \left< 3s_{1/2} \right| + \left( \frac{1}{2} \right)^{1/2} \left| 3s_{3/2} \right> \left< 3s_{3/2} \right| \). The transformation coefficients here and in the \( Y \) and \( W \) matrices come from Eq. 6.4.16 of Ref. [27].

We must now calculate the \( M_{k_p} \). They can be written as a product of a radial integral, an angular integral, an overlap integral, and a phase factor:
\[
M_{k_p} = \left< \phi_{k}^j \left| r \right| \left| J_0 \right> \left< \nu_k^j \left| v \right| \exp \left( i \pi r_{\rho}^j \right) \right|^\dagger \exp \left( i \sigma_j \right). \tag{A8}\]

\( \left< \nu_k^j \left| v \right> \) is given in Ref. [32] as
\[
\left< \nu_k^j \right| v = \frac{2 \nu_{k}^j \sin \pi \nu_{k}^j - \nu_k^j}{\nu_{k}^j \sqrt{2} (\nu_{k}^j - 1)} \times \tag{A9}\]

the first exponential of Eq. (A8), the \( r_{\rho}^j \) comes from the \( K \) matrices, as described in Ref. [19], \( \exp \left( i \sigma_j \right) \) is the Coulomb phase factor, in which \( l \) is the orbital angular momentum of the outgoing electron. This is 1 or 3 in our case. \( \sigma_j = \arg \Gamma \left( l + 1 - i/k \right) \), where \( k^2/2 \) is the kinetic energy of the free electron; i.e., \( k^2/2 = -E - E_{3s} \), in atomic units. \( C^{(1)} \) is the first-rank renormalized spherical harmonic tensor operator [28], such that \( r^{(1)} = C^{(1)} \). We have evaluated its matrix elements in \( jj \) coupling using Eq. 7.1.7 of Ref. [27] twice, which leads to the formula
\[
\left< (l_i' s_i') l_j' J'_j \left| r \right| (k^{(1)} = 1) \left| (j_i j_1 s_1) l_j s_j \right> \right.
\[
= X_{j_i j_1} \left( -1 \right)^{J_j + j_1 + j_2 + j_i + 1} \left[ J'_j J'_j \left| j_i j_1 \right| l_i' l_i j_1 \right| l_k \times
\[
\times \left| 0 0 0 \right| J j j j_1 \right| s_1 \right| l_i' l_k \right| \right. \tag{A10a}
\]
where \( X_{j_i j_1} \) is the radial integral. Since \( X \) is common to all of the \( M_{k_p} \), we ignore it from now on. (Here we make the good approximation that the radial integrals are equal for \( 3p_{1/2} \) and \( 3p_{3/2} \) states.) We find the \( M_{k_p} \) as shown in Table V.

To summarize this derivation, the \( M_{k_p} \), which are complex numbers, go into the summations of Eq. (A6), producing the reduced matrix elements \( D_{m_p} \), which are also complex numbers. Equation (9) uses these matrix elements to calculate the real angular distribution parameters \( \beta, \gamma, \alpha \) as a function of energy. The \( K \) matrices

<table>
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<th>TABLE V. The reduced matrix elements ( M_{k_p} ) used in calculation of the angular distribution parameters of the 3pnd states of Mg. We have evaluated the ( \arg \Gamma \left( l + 1 - i/k \right) ) in the Coulomb phase using Eqs. 6.1.15 and 6.1.24 of Ref. [33]. In this table we have excluded a common factor of ( \exp \left( i \arg \left( \Gamma \left( l + 1 - i/k \right) \right) \right) ) (and the radial integral) from all of the ( M_{k_p} ).</th>
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are slowly varying functions of energy; the energy dependence of $\beta$, $\gamma$, and $\epsilon$ comes primarily from the calculation of $\nu'$ and the rapidly varying phases $\tau'_o$.

The difference between theoretical parameters calculated in this appendix and the parameters calculated in Sec. III, is that here we use an earlier version of the $K$ matrices (the same as those used in Refs. [2,3,19], which are less accurate and also neglect the $3png J = 3$ channels. Although the MQDT analyses here and in Sec. III are quite different, they produce the same parameter values if the input $K$ matrices are the same. The differences shown in Figs. 4, 5, and 6 between the theoretical methods indicates the errors in the less precise $K$ matrices used in this appendix and in Refs. [2,3,19].