2-1995

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PHYSICAL REVIEW A VOLUME 51, NUMBER 2 FEBRUARY 1995

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(Received 19 September 1994)

Single-photon ionization of an atom or molecule can be subdivided into parity-favored and -unfavored transitions, the latter characterized by electron emission, preferentially perpendicular to the electric vector. The nonresonant existence of these transitions is shown experimentally and studied over an extended energy range for a variety of satellite transitions in atomic argon. The spectra exhibit several clearly resolved satellite lines with strongly negative β values close to -1, independent of the photon energy. The results confirm the corresponding predictions of angular-momentum transfer theory.

PACS number(s): 32.80.Fb, 32.80.Dz

Well above threshold, the angular distribution of photoelectrons resulting from a single ionization process follows the general interaction pattern of classical electromagnetic waves and free electrons, leading to electron emission, preferentially in the direction of the electric-field vector. This corresponds in terms of the angular-distribution asymmetry parameter β, describing the angular dependence of the differential photoionization cross section

$$\frac{d\sigma(h\nu)}{d\Omega}=\frac{\sigma(h\nu)}{4\pi}[1+\beta(h\nu)P_2(\cos\theta)],$$

to a value close to $\beta=2$. This is the upper limit of the asymmetry parameter if one restricts the differential cross section to physically meaningful positive values. However, a rigorous description of the photoionization process in terms of the associated angular-momentum transfer postulates the existence of a whole class of transitions showing exactly the opposite behavior; the corresponding photoelectrons are predominantly emitted orthogonal to the electric field [1], an emission pattern characterized by the lower limit of the asymmetry parameter $\beta=-1$. Such transitions, which are referred to as parity unfavored, are expected to exhibit this characteristic angular-distribution behavior always, independent of the excitation energy [2]. More specifically, angular-momentum transfer theory subdivides electric dipole transitions into two classes, depending upon whether the parity of the transferred angular momentum is favored or unfavored. It is the parity of the angular momentum transferred from the target to the residue, $\mathbf{j}_t=\mathbf{j}_\gamma-l=\mathbf{L}_f-\mathbf{L}_i$, which determines the photoelectron angular distribution. Here $j_\gamma=1$ for electric dipole processes, l is the orbital momentum of the photoelectron, and L_i and L_f are the unobserved momenta of the target and residue (including the unobserved spin of the observed electron); conditions of parity favoredness or unfavoredness exist when the parity of the transferred angular momentum is either even or odd, respectively. More specifically, a parity-favored electric dipole transition, for which j_t+1+l is supposed to be even, always has two possible values of j_t $(=l\pm 1)$. In the case of odd parity this choice is diminished; only one value of j_t $(=l)$ is allowed, becuase additional angular momenta of the same symmetry are prohibited due to dipole selection rules; hence, the name parity unfavored. In other words, for a parity-unfavored transition, the angular momenta of the electron and photon couple in such a way that no angular-momentum component of the photon is transferred to the electron, which means that the momentum transferred between the atom and the ion $\mathbf{j}_t$ becomes equal to the electron momentum l. Thus, the angular distribution asymmetry parameter β_{unf}, becomes automatically -1 because the momentum projection along the photon quantization axis is zero. In contrast, due to the ambiguity of the two outgoing channels, parity-favored transitions can have any asymmetry parameter between the extremes -1 and 2, depending on the specific dynamics. Since the first prediction of parity unfavoredness in the distribution of photofragments two decades ago by Dill and Fano [2], the corresponding transitions have been a subject of continuous interest in a variety of fields. Clear evidence for the existence and importance of parity-unfavored transitions has been found, e.g., for s-subshell photoionization [3], particularly in Cooper minima [4,5], autoionization [6,7], and Auger decay of resonances [8–14], and in the behavior of slow photoelectrons, particularly near the threshold for double photoionization [15,16]. However, in the clearest manifestation of these transitions, their nondegenerate occurrence in nonresonant photoionization has never been proven experimentally. For this reason parity unfavoredness in photoionization was largely viewed as a resonant and near-threshold phenomenon. In this Rapid Communication we show clear evidence for the nonresonant appearance of photoelectrons resulting from purely parity-unfavored transitions over an extended excitation energy range. We show that these photoelectron lines are indeed predominantly emitted perpendicular to the electric field, independent of the excitation energy, as predicted by angular-momentum transfer theory.

One reason why parity-unfavored transitions have achieved so little attention despite strong theoretical interest

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in the underlying pseudovector or pseudotensor interactions between the observed and unobserved reaction products is the fact that these transitions for main-line photoionization are realized only in open-shell atoms. In closed-shell atoms parity-unfavored transitions are always associated with two-electron transitions; otherwise the necessary reaction balance concerning angular momentum and parity cannot be fulfilled. Keeping this in mind, two possible cases of parity unfavoredness are easily depicted; in one case odd states of D symmetry require an εd electron, in the other case even states of P symmetry require an εp wave. More specifically, in the case of argon this is shown by

$$3s^2 3p^6(^1S) + h\nu \rightarrow 3s^2 3p^4(^3P)3d(^2P) + \varepsilon p,$$

$$\Delta L = 1, \quad \Delta\pi = +1 \text{ in the ionic core} \tag{1a}$$

$$\rightarrow \text{ Parity of outgoing electron: } \pi_e = -1,$$

$$3s^2 3p^6(^1S) + h\nu \rightarrow 3s^2 3p^4(^3P)4p(^2D^0) + \varepsilon d,$$

$$\Delta L = 2, \quad \Delta\pi = -1 \text{ in the ionic core} \tag{1b}$$

$$\rightarrow \text{ parity of outgoing electron: } \pi_e = +1.$$

In both cases there is only one outgoing electron wave because the parity requirement inhibits the existence of another ionized channel along with the dipole selection rules.

Although there are many possible transitions of this kind, there has been only scant evidence of the existence of the corresponding transitions in photoelectron spectra. The clearest evidence for parity-unfavored transitions came from resonance enhancement in autoionizing resonances [6–14]. Here the appearance of lines with strongly negative β could be attributed clearly to parity-unfavored transitions strongly enhanced on resonance by the Coulomb interaction, which has no directional preference, as in the case of the electric-field vector in direct photoionization.

In many cases where parity-unfavored lines have been observed in photoelectron spectra it was found that they were still resonantly enhanced, as for example the Ar $(^3P)4s(^2P)$ satellite state [17]. Only recently did a nonresonant high-resolution satellite spectrum of atomic argon taken at 40.8 eV reveal several clearly resolved lines that were attributed to parity-unfavored transitions [18]. However, no proof of the predicted characteristic angular distribution pattern was available because the asymmetry parameter was not measured. Another recent high-resolution study that measured the angular distribution gave no definite β values for the transition of interest [19]. Furthermore, all these studies were restricted to one or a very few photon energies in or near the region of possible resonances due to double excitations. Therefore, it could still be that pure parity-unfavored transitions outside of resonances are not realized in nature because of the orthogonality between the electric-field vector and the electron emission direction that tends to suppress such transitions well above threshold. In order to look more carefully into the possible nonresonant existence of these transitions we have studied the angular distribution of satellite lines in atomic neon and argon.

The experiments were performed at the Berliner Speicherring Gesellschaft for Synchrotronstrahlung, BESSY, under

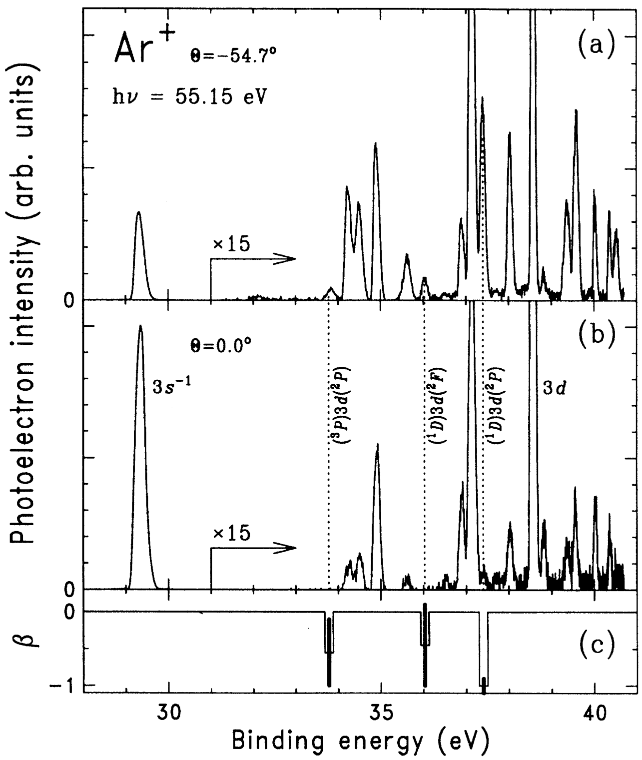

FIG. 1. Valence satellite spectra of argon taken at a photon energy of $h\nu = 55$ eV under and angle of (a) 54.7° and (b) 0° with respect to the electric vector. The parity-unfavored transitions are marked by dotted lines in addition to their specific designation and the β values in the lower panel (c) of this figure. Only the $3s^{-1}$ main line and the first $3d$ correlation satellite are particularly labeled.

single bunch conditions behind the undulator beamline U1 [20]. Monochromatic photons from a toroidal grating monochromator (TGM-5) with a resolving power of approximately 600 were employed to ionize an effusive beam of rare-gas atoms. Emitted photoelectrons were detected by two time-of-flight electron spectrometers positioned at two different angles. In order to measure the angular distribution at more than two angles, the two detectors were rotated simultaneously. The whole apparatus has been described in more detail elsewhere [21]. For the experiments reported here, searching for weak signals in a complex photoelectron spectrum, the combined energy resolution, photon flux, and detection efficiency of both monochromator and electron spectrometer were crucial. Figure 1 shows two photoelectron spectra of argon taken at $h\nu = 55$ eV at 54° and 0° with respect to the electric vector. The dotted lines represent clearly resolved satellite transitions which are designated as parity-unfavored transitions. This designation is corroborated nicely by their characteristic angular distribution behavior, as shown exemplarily in Fig. 2 for one of the satellite states. The three transitions belong to the following final ionic states: $(^3P)3d(^2P)$, $(^1D)3d(^2P)$, and $(^1D)3d(^2F)$. These states are most likely populated via an ISCI-FISCI mechanism (intial-state/final ionic-state configuration interaction) showing strongest intensity for the states

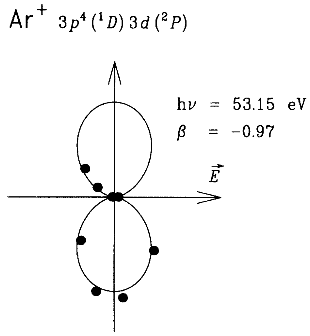

FIG. 2. Characteristic photoelectron angular distribution pattern for the parity-unfavored transition $3p^4(^1D)3d(^2P)$ at $h\nu = 53$ eV.

with lowest angular momentum [22]. Figures 3–5 show the partial cross section and angular asymmetry parameter β of these three satellite lines in the photon-energy range between 34 and 60 eV. There are three characteristic features displayed by all three satellites: (i) strongly negative β values that are excitation energy independent, as predicted by angular-momentum transfer theory; (ii) strong resonance enhancement near threshold due to double excitations; and (iii) nonresonant behavior of the cross section that mimics that of one of the main lines, $3s$ or $3p$, supporting the ISCI-FISCI model.

The second point was the subject of a series of detailed studies in all rare gases [23–25], showing the difficulties in the differentiation between nonresonant and resonant behavior. Figures 3–5 show considerable satellite intensities at several excitation energies outside the double-excitation region. This, along with the measured angular anisotropies,

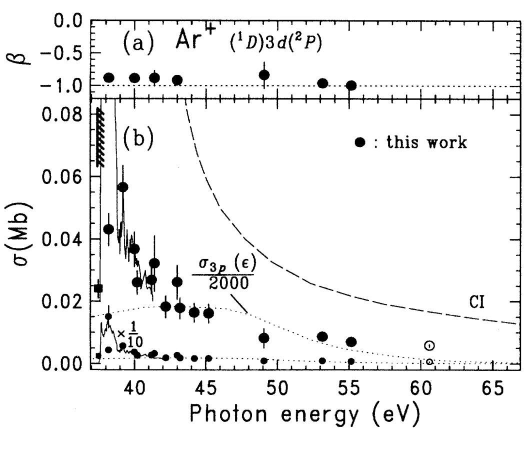

FIG. 3. (a) Angular distribution parameter β and (b) partial cross section σ of the $3p^4(^1D)3d(^2P)$ parity-unfavored satellite transition in argon ($E_B = 37.4$ eV). The resonance structure in the partial cross section from Wills *et al.* [25] is adjusted to the absolute values of our data at the high-energy end. The dotted curve represents the $3p$ partial cross section scaled to the satellite intensity at equal kinetic energy. The dashed curve shows the configuration-interaction calculation of Sukhorukov *et al.* [27], the open circle is measured by Krause *et al.* [19], and the filled square is a zero kinetic energy point from Heiser *et al.* [24].

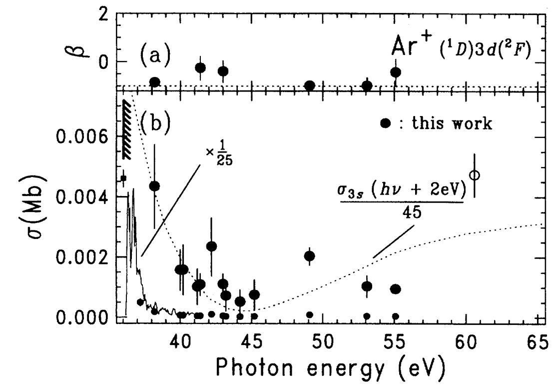

FIG. 4. (a) Angular distribution parameter β and (b) partial cross section σ of the $3p^4(^1D)3d(^2F)$ parity-unfavored satellite transition in argon ($E_B = 36.0$ eV). The dotted curve represents in contrast to Fig. 2 the $3s$ partial cross section instead of $3p$. The resonance structure in the partial cross section is, as in Fig. 2, from Wills *et al.* [25], the open circle and the filled square are from Krause *et al.* [19] and Heiser *et al.* [24].

corroborates the predictions of the angular-momentum transfer theory concerning parity unfavoredness in photoionization. All the examples shown here belong to case (a) transitions with odd photoelectron angular momenta, but there are clear indications that cases with even angular momenta such as case (b) do exist; however, they remain still unresolved from closely lying parity-favored transitions. A case where a parity unfavored transition occurs only on resonances is the transition to the $(^3P)4s(^2P)$ final ionic state. But this behavior is less related to the unfavoredness of the transition rather than to the ISCI-FISCI mechanism of satellite production. The ^3P-coupled parent state has even parity and thus cannot be involved in transitions to a $3p^44s$ configuration. This is the reason why these states are clearly observed in the fluorescence spectrum [17,26] and also in threshold [23,24] or near-threshold spectra [25], being affected by autoionizing resonances, where other selection rules apply. It is noteworthy to mention that additional measurements on the corresponding transition in neon populating the $(^3P)3s(^2P)$ final

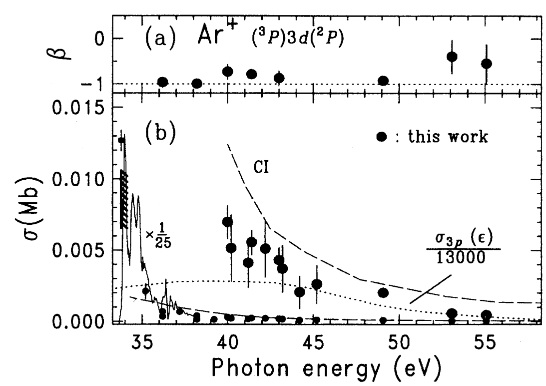

FIG. 5. (a) β and (b) σ of the $3p^4(^3P)3d(^2P)$ parity-unfavored satellite transitions in argon ($E_B = 33.76$ eV). All other explanations are like in Fig. 2.

ionic state show not only strong resonance enhancement, but also measurable nonresonant intensity with strongly negative β values for all excitation energies, resonant and nonresonant. Here, another satellite production mechanism, perhaps conjugate shakeup, seems to contribute to the parity-unfavored satellite intensity [7]. More detailed theoretical investigations have to be performed to explain this different behavior in two isoelectronic configurations concerning the resonant and nonresonant occurrence of parity-unfavored transitions. First attempts in this direction employing the configuration-interaction method where undertaken by Sukhorukov *et al.* [27]. The present study suggests that nonresonant parity-unfavored transitions are a natural phenomenon in atomic photoionization that are to be expected in all elements, but still unobserved in heavier elements such as Kr and Xe due to insufficient resolution. However, one should keep in mind that the number of possible parity-unfavored transitions in closed-shell atoms is quite limited compared to the number of parity-favored transitions, depending on the satellite production mechanism. This is simply a consequence of the reaction balance, giving more coupling opportunities for a favored than an unfavored angular-momentum transfer between the reaction products rather than the character of the unfavoredness itself. Once, the transition is made possible via a certain mechanism, it has the same strength as it would have under favored conditions.

In summary, we have shown that parity-unfavored transitions do exist in nonresonant photoionization, as postulated by angular-momentum transfer theory. The characteristic angular distribution of $\beta=-1$ corresponding to preferential electron emission perpendicular to the electric vector was demonstrated for several transitions and an extended range of excitation energies. The results suggest that these transitions are quite natural in nonresonant photoionization and are expected to occur in most elements; in particular in all open-shell systems, with considerable strength.

This work was funded by the Bundesminister für Forschung und Technologie.

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