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Near-100% production of the excited Be^+ $1s\,^2 2p$ ion from decay of Be $1s2s\,^2 2p$

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In examining the decay of photon-produced Be $1s2s^2np(^1P)$, $n=2,3$, we discovered that the vastly predominant decay mode is to the final excited ionic states Be^+ $1s^2np$, rather than the ground state. For $n=2$, the $2p$ ion accounts for 95% of the total production, with Be^+ $1s^23p$ the other main contributor. For $n=3$, $3p$ is predominant, again with a very small fraction of $2s$. The result for $n=2$ occurs as a consequence of the similarity between the $2s$ and $2p$ radial wave functions of the excited state, which leads to a cancellation in the amplitude for transition to the $2s$ ground state.

An atom which is excited by a photon or by electron bombardment to a state which lies above the first ionization potential decays preferentially by electron emission. The decay to the ground state of the ion is generally strongest, but it is common that one or more excited-state ionic channels can be populated via electron correlation. This leads to satellites which accompany, but are usually weaker than, the principal decay. However, in some instances of excitation, the excited electron appears not to participate strongly in the decay process, leading to an enhancement of the production of excited-state ions relative to that of the ground-state ions.[1]

In our experiment on the decay of excited states of beryllium of the type $1s2s^2np$ we obtained an excited-state:ground-state ratio of ions which is not in accord with expectations based on models derived from previous results.[1,2] Rather than a noticeable amount of ground-state ions with a normal enhancement of excited-state species, we discovered an overwhelming *predominance* of the excited state at every $1s2s^2np$ excitation we examined. For $n=2$, the $2p$:$2s$ intensity ratio is 55 ± 3; for $n=3$, the $3p$:$2s$ ratio is about 78; yet only the $3p$:$2s$ ratio can be rationalized as a "spectator" phenomenon.[2]

The experiment was performed using the 3-m toroidal grating monochromator at the University of Wisconsin Synchrotron Radiation Center. The beryllium atoms were created by evaporation of solid Be in a newly designed vapor oven which serves also as the electron source for the electron analyzers. The oven was operated typically at 1010 °C, providing a vapor pressure in the low range of 10^{-3} Torr. The signal level attainable with this new source allowed us to operate with a monochromator bandpass as low as 0.4 Å, although most data were recorded at a bandpass of 0.7 Å. The electrons were energy analyzed in a spherical sector plate analyzer having a resolution $\Delta E/E=1\%$ and detected at an angle of 55° with respect to the major polarization axis of the photon beam so as to avoid the influence of the angular distribution on the intensities.

Photoelectron spectra were recorded in both the PES (photoelectron spectroscopic) and CIS (constant ionic state) modes.[3] In the former, spectra of Be^+ final states were recorded at the $1s\rightarrow 2p$ and $1s\rightarrow 3p$ resonance energies. In the latter, the photon and electron analyzer pass energies were scanned simultaneously through the $1s2s^2np$ excitation region from $n=2$ to $n=\infty$, and contributions to the various final ion states, Be^+ $1s^22s$, $1s^22p$, and $1s^23p$ were recorded. The excitation energies of the $1s2s^2np$ ($n=2,3$) levels were measured in the CIS mode, and our results were found to agree well with previous data[4,5] and with calculations.[6] While our bandpass was adequate to be able to observe the ^3P level, we found no trace of it, so our results are restricted to the ^1P level.

In Fig. 1 are shown the results of our PES scans at photon energies corresponding to $1s$-$2p$ excitation at 115.5 eV and $1s$-$3p$ excitation at 121.4 eV. The identifications of the final ionic states are given at the top. The curves have been normalized to the same vertical scale so that the integrated count under each curve gives the relative contribution of that final state to the decay rate. The striking feature of this result is the magnitude of the Be^+ $1s^22p$ peak in Fig. 1(a) compared to the remainder, particularly Be^+ $1s^22s$, which is barely visible in the original trace. An expansion of the y scale reveals the presence of contributions to the $1s^23p$ and higher np levels. Specifically, we find the $1s^22p$ percentage to be 95% of the entire decay of the $1s2s^22p(^1P)$ excited state.

The predilection of the Be $1s2s^2np$ excited state to decay into corresponding Be^+ $1s^2np$ ionic states continues into the $n=3$ excitation as well; see Fig. 1(b). In this case the predominance of $3p$ is again pronounced compared to the ground state. However, the higher $1s^24p$ state has now gained greater importance.

In Fig. 2 are shown the results of CIS scans, panels (a) to (c), corresponding to production of the Be^+ $1s^22s$; $1s^22p$; and $1s^23p$ states of the ion. For these data the

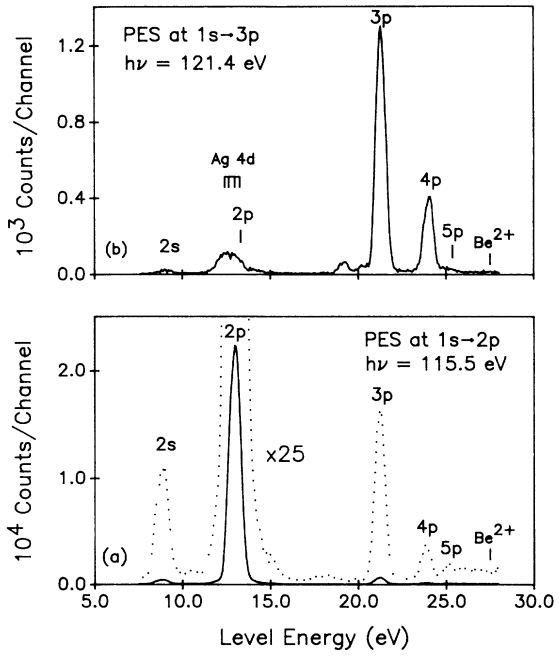

FIG. 1. Electron spectra resulting from the decay of the Be $1s2s^2np(^1P)$ excited states. (a) $n=2$, $h\nu=115.5$ eV; (b) $n=3$, $h\nu=121.4$ eV. The $3p$ spectrum shows some contamination of the Be^+ $1s^22p$ peak due to the presence of silver in the oven. Note the predominance of the Be^+ $1s^2np$, $n=2,3$, final states of the ion, and the very small amount of Be^+ $1s^22s$.

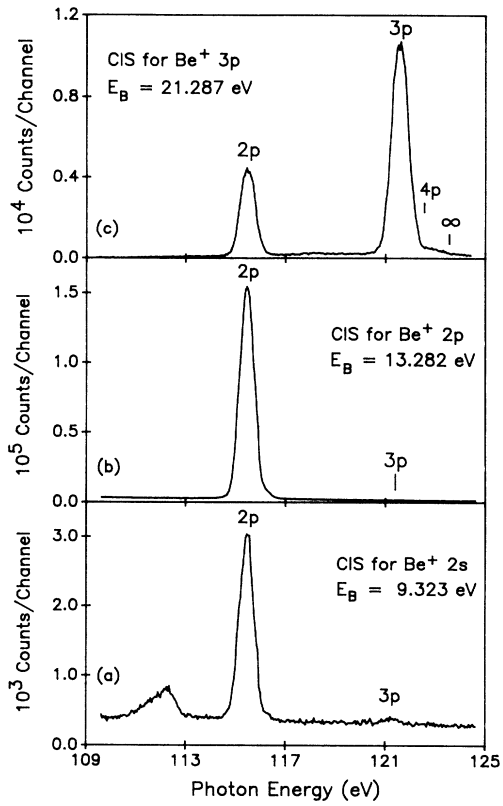

FIG. 2. Constant ionic state (CIS) spectra for three different ionic states: (a) Be^+ $1s^22s$; (b) Be^+ $1s^22p$; and (c) Be^+ $1s^23p$. The intensities have been adjusted by normalization with PES spectra. Note the factor of 100 difference between (a) and (b). The predominance of Be^+ $1s^22p$ at $h\nu=115.5$ eV is clearly visible. The structure in (a) near 112 eV is presumably due to a resonance scattering process. Each spectrum contains 300 channels.

photon energy was scanned over a range that includes all $1s2s^2np$ excitations. The important $2p$ and $3p$ excitations are marked at the top of the figure. The vertical scales have been adjusted to give the proper ratios as determined from the PES data. While at each resonance an enhancement occurs in the ground-state $2s$ channel, its magnitude is much less than for the p channels. The "background" levels correspond to the partial cross sections outside the resonances.

The results for both the PES and CIS scans are summarized in Table I. We note that off resonance, the ionization behaves in accordance with an initial-state configuration interaction (ISCI) approach. We observe a $2p$:$2s$ ratio of $\sim$12:100, which is indicative of the admixture of p^2 in the ground-state atomic configuration. This value is in agreement with multiconfiguration Hartree-Fock calculations for Be K-shell photoionization.[7]

One may understand the large observed ratio of $2p$:$2s$ production using an analog of the compound nucleus model for resonant nuclear scattering,[8] i.e., assuming the decay of the Be $1s2s^22p(^1P)$ state is independent of its formation. The relative intensities of the Be^+ $1s^22p(^2P)$ and Be^+ $1s^22s(^2S)$ final ionic states are then proportional to the squares of the following Coulomb matrix elements:

$$V_{2p}\equiv\left\langle 1s2s^22p(^1P)\left|\sum_{i>j}\frac{1}{r_{ij}}\right|1s^22p(^2P)\varepsilon s(^1P)\right\rangle=-\int dr_1\int dr_2 P_{1s}(r_1)P_{\varepsilon s}(r_2)r_>^{-1}[P_{2s}(r_1)P_{2s}(r_2)]\,, \tag{1}$$

$$V_{2s}\equiv\left\langle 1s2s^22p(^1P)\left|\sum_{i>j}\frac{1}{r_{ij}}\right|1s^22s(^2S)\varepsilon' p(^1P)\right\rangle$$

$$-\int dr_1\int dr_2 P_{1s}(r_1)P_{\varepsilon' p}(r_2)r_>^{-1}[P_{2s}(r_1)P_{2p}(r_2)-(2r_</3r_>)P_{2s}(r_2)P_{2p}(r_1)]\,. \tag{2}$$

In Eqs. (1) and (2), both initial and final states are described by a single configuration. The right-hand side represents the matrix element in terms of radial Slater integrals over the one-electron radial wave functions $P_{nl}(r)$; ε and ε' are the continuum kinetic energies of the photoionized electron for each of the two final ionic states. Finally, $r_>\equiv\max(r_1,r_2)$ and $r_<\equiv\min(r_1,r_2)$.

One sees clearly from Eqs. (1) and (2) that where the

TABLE I. Relative contribution of the final-state decay channels (rows) as a function of the excitation (columns).

	Resonance transitions	
$Be^+ 1s^2nl$	$1s \rightarrow 2p$	$1s \rightarrow 3p$
$2s$	1.8(1)	0.1
$2p$	100.0[a]	<0.4[b]
$3p$	2.86(7)	7.8(3)
$4p$	0.47(4)	2.2(3)
$5p$	0.16(4)	0.1

[a]Normalization point, Ag contribution is less than 0.5%.
[b]Ag $4d$ interferes strongly.

TABLE II. Widths Γ for nonradiative decay of Be $1s2s^2np(^1P)$ resonant states to $Be^+ 1s^2np$ and $Be^+ 1s^22s$.

	Decay width (a.u.)		Ratio
Resonant state	Γ_{np}	Γ_{2s}	Γ_{np}/Γ_{2s}
$2p$[a]	1.2×10^{-3}	5.0×10^{-5}	24
$2\bar{p}$[b]	1.4×10^{-3}	4.6×10^{-5}	31
$3p$[a]	1.3×10^{-3}	5.3×10^{-6}	250
$3\bar{p}$[b]	1.7×10^{-3}	4.7×10^{-6}	360

[a]Resonant state treated as a single configuration, Be $1s2s^2np(^1P)$.
[b]Resonant state treated as a linear combination of the configurations Be $1s2s^2np(^1P)$ and Be $1s2p^2np(^1P)$.

Coulomb repulsion between the jumping electrons is largest, i.e., $r_1 = r_2$, V_{2p} has its maximum value [with the factor in brackets $\propto P_{2s}^2(r)$] while V_{2s} has extensive cancellation [with the factor in brackets $\propto P_{2s}(r)P_{2p}(r)/3$]. Because of this factor $\frac{1}{3}$ in V_{2s} for $r_1 = r_2$, we expect the squares of Eqs. (1) and (2) to differ by an order of magnitude. As discussed "in physical language" for a similar case in He,[9] "an electron can be propelled by Coulomb repulsion to the high speed of the free εl state only in a region sufficiently close to the other electron."

This expectation is easily confirmed numerically using a basis of bound Hartree-Fock (HF) wave functions calculated for the Be $1s2s^22p(^1P)$ resonant state as well as HF continuum orbitals εs and εp calculated in the field of the appropriate relaxed Be^+ state. Effects of nonorthogonal overlap integrals are included.[10] The $1s$, $2s$, and $2p$ orbitals are shown in Fig. 3. Clearly the region $r_1 = r_2 = 1.8$ is where P_{2s} and P_{2p} have their maximum values. As shown in Table II, use of these wave functions leads to a ratio of 24 for the Be^+ $2p$ to $2s$ final ionic states.

Matrix elements similar to those in Eqs. (1) and (2) apply for the resonant state Be $1s2s^23p(^1P)$. V_{3p} has the same analysis as V_{2p}. However, the analysis of V_{2s} requires more care since the first two antinodes of P_{3p}, shown in Fig. 3, are both relevant. Such an analysis leads one again to expect that the square of V_{2s} is at least an order of magnitude smaller than the square of V_{3p}. The results in Table II reveal it is 2 orders of magnitude smaller, giving a $3p$:$2s$ ratio of 250.

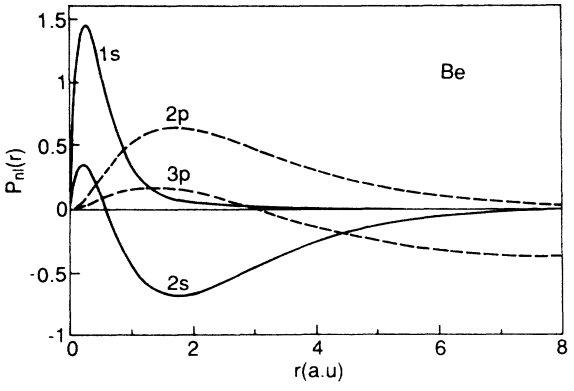

FIG. 3. Radial orbital wave functions for $1s$, $2s$, and $2p$ in Be calculated in HF approximation for the state Be $1s2s^22p(^1P)$. The $3p$ orbital shown is calculated for the state Be $1s2s^23p(^1P)$.

More accurate estimates for the branching ratios can be obtained by including the dominant configuration mixing in the resonant state, namely, $2s^2 \leftrightarrow 2p^2$. Thus, we have considered the resonant state for the case of $2p$ to be (0.962) Be $1s2s^22p(^1P) + (0.273)$ Be $1s2p^3(^1P)$; similar configuration mixing for the $3p$ case was also included, as indicated in Table II. In each case, the decay widths for np increase and those for $2s$ decrease so that the branching ratios increase to 31 for $2p$:$2s$ and to 360 for $3p$:$2s$. Finally, we have also calculated the photoionization cross sections for populating the different final states. Whereas the $2p$:$2s$ branching ratio is unchanged, the $3p$:$2s$ branching ratio for the $1s2s^23p$ resonance is reduced to approximately 200 since the direct photoionization amplitude is not negligible compared to the resonant amplitude, as shown experimentally in Fig. 2(a).

Our first-order calculations ignore the large-scale configuration interactions in initial and final states which may be necessary[10-12] to make detailed comparisons with experimental inner-shell spectra such as those presented here. Such an extensive calculation for Be has been carried out by Mercouris and Nicolaides.[11] However, while their results agree with the experimental $3p$:$2s$ ratio, they obtain, remarkably, an order of magnitude smaller value for the $2p$:$2s$ ratio than experiment indicates.

While our excited-state population for $n=2$ is considerably larger than those obtained in related experiments,[1,2] there exists an experiment[13] that gives possible evidence of a greater than "normal" population. For Be-like $O^{4+} 1s2s^22p(^{1,3}P)$, a value of 16 ± 10 was reported for the $1s^22p$:$1s^22s$ ratio arising from the (^1P) state, but only 1.7 from the (^3P) state. For the (^1P) state, the large error did not allow an unambiguous statement.

In conclusion, we report experimental evidence for the unusually strong population of an excited ionic state from the decay of an autoionizing state for which the ordinary spectator model does not apply. Instead, our calculations show that a cancellation in the transition amplitude to the ground state is responsible for this phenomenon. Apart from its intrinsic physical interest, the phenomenon is also

of practical importance, as it could serve as a means for selective production of excited-state ionic species with high purity.

Note added: Following submission of the manuscript, we learned that D. Petrini (personal communication) has calculated values for the $Be^+ 1s^2 2p$:$Be^+ 1s^2 2s$ intensity ratio which agree well with our experimental data. These R-matrix results confirm our interpretation and improve on the predictions made on the basis of our one- and two-configuration Hartree-Fock treatments. In addition, an earlier calculation for the analogous B^+ case [D. Petrini, J. Phys. B **14**, 3839 (1981)] indicates that the behavior we demonstrate and interpret for Be can be regarded as a common feature for the Be-like series.

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