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Atomic Electron Correlation in the *M* Capture of ^{37}Ar

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The first experimental evidence for electron correlation in nuclear electron-capture ratios is reported. The measured M/L capture ratio of ^{37}Ar, 0.073 ± 0.007, is inconsistent with Hartree-Fock calculations, but can be explained by final-state correlation, if the disputed $3s3p^6$ assignment in Cl I is adopted. The discrepancy in the experimental $K\beta/K\alpha$ x-ray intensity ratio of Cl is removed, and the designation of L_{23} x-ray and $3s$ photoemission satellites in Cl is revised.

The inclusion of the atomic electrons in the calculation of nuclear electron-capture (EC) probabilities leads to exchange-overlap factors.[1] Recently, EC ratios were recalculated according to the independent-particle approaches of Bahcall[2] and Vatai,[3] and, for M/L ratios (P_M/P_L), fair agreement was stated between experiment and Vatai's approach, which neglects shakeup and shakeoff.[1] More recently, a first calculation that took correlations into account[4] gave an ^{37}Ar M/L ratio of 0.102 (Bahcall, 0.129; Vatai, 0.115),[1] which was in excellent agreement with experiment[5] ($0.104^{+0.006}_{-0.003}$).

This Letter reports on a new experiment which yields 0.073 ± 0.007 in strong contrast to this result. It is shown that the independent-particle model breaks down in ^{37}Ar M capture and that the measured spectra have been drastically misinterpreted. Moreover, the previous experimental value[5] turns out to be spurious, so that agreement with theory[4] can only be fortuitous. The observed correlation effect corresponds to correlation in the optical spectrum[6,7] of Cl I and in atomic processes[8-12] leading to the same final state as ^{37}Ar M capture.

Both experiments were performed with proportional counters.[5,13] The spectra are dominated by two overlapping pulse distributions, the L-capture peak and a single-electron spectrum[14] (Fig. 1). Renier *et al.*[5] identified the latter with M capture on assuming that each M event entailed the

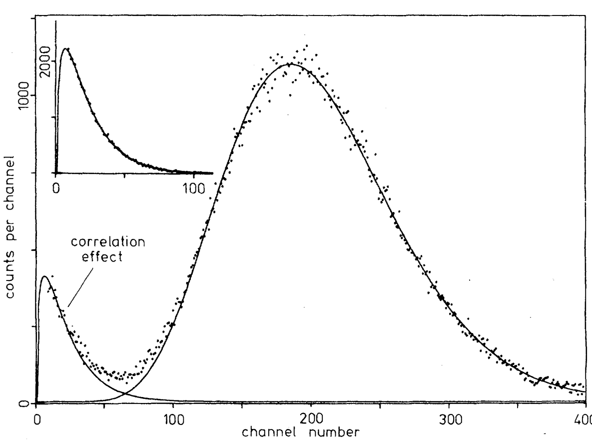

FIG. 1. M-L spectrum of ^{37}Ar (pressure: 4 bars), background subtracted. The extrapolated K degradation tail is drawn in as pedestal of the fitting curves. L degradation is not marked for clarity. The L peak is fitted by a Γ (Ref. 15), the M peak by a Polya distribution (Ref. 14); the latter was determined from a single-electron spectrum (inset) due to photoelectrons released in the counter by uv irradiation (the peaked shape was confirmed at higher sensitivity).

emission of one Auger electron of ~5 eV.[1] This, however, appears to be unfounded (see below).

In addition, the analysis of the experiment[5] is incorrect. (1) In order to allow for x-ray escape, P_M/P_L and k_β/k_α, the $K\beta/K\alpha$ x-ray intensity ratio of Cl, were determined as the solutions of a set of equations established from measurements at various pressures. This procedure included the erroneous assumption that each $K\beta$ x-ray escape simulated a spurious M event, which, in fact, only occurs with ~5% probability by the radiative Auger effect.[16] As a consequence, the resulting k_β/k_α value of 0.020 ± 0.015 is too low. It disagrees with a later measurement ($0.095\pm 2\%$) and with theory (0.086).[17] Removing the error reveals inconsistencies: The solutions are $P_M/P_L=0.108$ and the most improbable $k_\beta/k_\alpha=0.45$; on the other hand, evaluating P_M/P_L using $k_\beta/k_\alpha=0.09$ yields systematically higher values at low pressure (0.117 at 0.5 bar). (2) L-pulse degradation was neglected, though K degradation was significant. A fraction f of the L events was probably evaluated as M events simulating too low $K\alpha$ escape. This causes an underestimation of k_α or, if k_β/k_α is fixed at 0.09, overestimation of P_M/P_L, especially at low pressure [see (1)]. With $f=1.25\%$, these inconsistencies vanish, and we have the solutions $P_M/P_L=0.096$, $k_\beta/k_\alpha=0.09$. (3) The exponential extrapolation of the M spectrum to zero energy might have slightly overestimated P_M/P_L, since a Polya distribution probably is appropriate.[14] Reevaluation suggests $P_M/P_L\approx 0.090-0.096$. The method of measurement is unsuitable to determine k_β/k_α because of its sensitivity to f ($0.45\geq k_\beta/k_\alpha\geq 0.09$, if $0\leq f\leq 1.25\%$). The discrepancy in the $K\beta/K\alpha$ ratio of Cl is thus removed.

The present experiment[13] was performed by means of a multiwire counter (Ar-10%CH_4) applying the usual counting procedure.[1] As pulse degradation[1] was almost negligible (0.3%) and the L and M peaks were well resolved (Fig. 1), no serious uncertainty arises from the M-L separation in this experiment. In the overlapping region, an amount of 0.8% of the L counting rate was not reproduced by the fitting curves. This remainder must be treated as degraded L pulses or as M-shell shakeoff in M capture resulting in $n\geq 2$ primary electrons. If we identify the single-electron part with the M capture events,[5] we get $P_M/P_L=0.069\pm 0.003$; if we include M pulses originating in $n\geq 2$ primary electrons, the result is 0.073 ± 0.007. The error contains the statistical error and, by linear addition, the maximum uncertainty of the M-L separation (± 0.006). After numerous experimental checks, I can imagine no error that might significantly have affected the result. An important loss of primary electrons by attachment or recombination is unlikely from energy resolution arguments.[13]

Vatai's basic assumption, the neglect of shakeoff,[3] fails in ^{37}Ar M capture: The change in nuclear charge is poorly compensated by the 3s vacancy, so that the M electrons, by Slater's rule, see an effective $\Delta Z_{\rm eff}=-0.65$. According to the energy distribution of shakeoff electrons,[18] M-shell shakeoff in M capture contributes to the measured M peak, and has to be included in the calculations, while shakeoff from inner shells has to be omitted. I estimated shakeoff probabilities in EC by extending an empirical rule[18] to EC (in sudden approximation, the only relevant parameter is $\Delta Z_{\rm eff}$). The sign of $\Delta Z_{\rm eff}$ was considered in the way suggested by calculations for Kr $\beta^\pm$ decay.[18] Thus, from β^- decay and photoionization data,[18,19] the M shakeoff probability in M capture λ_{MM} was estimated at 10–20%, which is nonnegligible. Bahcall[2] allowed for shakeoff by applying closure. This requires corrections for the inclusion of 2p and the neglect of 3s shakeoff; they are ~2%, and tend to cancel. It should be noted that the absence of 4s electrons is advantageous and that the remaining simplifications can cause no serious error. In particular, applying closure does not overestimate the M/L ratio as was asserted.[1] From Bahcall's and Vatai's exchange-overlap factors,[1] one obtains $\lambda_{MM}=14.5\%$, i.e., $P_{MM}/P_L=0.019$ (P_{MM} is the EC probability to MM vacancy states), which is consistent with the above estimate. Shakeoff in L capture is of minor importance (~2%). I assert that, within the independent-particle model, Bahcall's *Ansatz* adequately describes the ^{37}Ar M/L ratio.

The position of the Cl I $3s3p^6$ level is crucial for the interpretation of the measured M spectrum. It had been identified, on the basis of isoelectronic extrapolation, with a new level at 10.62 eV most probably of ^2S symmetry.[20] Hartree-Fock (HF) calculations, however, place $3s3p^6$ at 15.5 eV, i.e., above the second (^1D) ionization limit, and configuration interaction (CI) with the bound $(^1D)nd\,^2S$ states pushes it still higher.[6,21] Hence, the above identification was questioned.[21] Cowan *et al.*[6] showed that CI with the $\epsilon d\,^2S$ continuum shifts the dominant $3s3p^6$ character to the lowest $J_{1/2}$ level at ~10.9 eV. Multiconfiguration HF (MCHF) calculations likewise yielded a dominant $3s3p^6$ nature for the lowest ^2S level and positions at 9.5 (Ref. 7) and 10.6 eV.[22]

A pure independent-particle treatment predicts $3s3p^6$ (15.5 eV) to be LS-allowed autoionizing. All M-capture events should produce at least one primary electron and be detected. Bahcall's approach applies, and predicts $P_M/P_L = 0.129$.[1] On the basis of the spectroscopic designation,[20] however, autoionization of the $3s3p^6$ state is energetically impossible. The photons emitted (10.6 eV) cannot ionize the counter gas,[23] and the electron yield from the walls is negligible, especially in a multiwire counter. Thus, only the M-capture transitions accompanied by shakeoff are detected,[24] and theory predicts $P_{MM}/P_L = 0.019$. It follows that experiment is inconsistent with the independent-particle calculations.

As $3s3p^6$ is mixed in the whole $3s^2 3p^4(^1D)nd$, $\epsilon d\ ^2S$ series,[6] M capture leads to all members of the series because of their $3s3p^6$ nature. All bound levels with $n \geq 4$ lie above the first $(^3P_2)$ limit,[6,20] and may be subject to autoionization. In fact, none of them have been found in emission.[20] They are rather pure LS states,[6] and autoionization is not allowed in LS coupling. J_cK coupling, however, is equivalent in this case, and interaction is possible with the $(^3P_2)\epsilon d, 2[0]_{1/2}$ continuum, the states of which are expected to have predominantly J_cK coupling.[20] Besides, other $(^3P_2)\epsilon s, \epsilon d$ continua with $J = \frac{1}{2}$ and even parity are attainable.[20] Spectroscopic evidence for autoionization in the $(^1D)nd$ series exists indeed, but the ^2S series is not resolved.[25,26] On the basis of the accumulated evidence, I assume tentatively that the $nd\ ^2S$ states autoionize effectively. Thus, all final states, *except* $3s3p^6$ and $3d\ ^2S$, were detected with the Ar-CH_4 counter, and also some fraction of the photons from the $3d\ ^2S$ state with the Ar-C_3H_8 counter.[23] Previous comparison between experiment and theory supposed that the $3s3p^6$ transitions were detected.[1,4]

Bahcall's *Ansatz* can be extended to include finan-state correlation (FSC). Let ψ_0 be the configuration-state function (CSF) for the Cl I state $3s3p^6$ constructed from HF or HX[6] orbitals and $\{\psi_i\}$ a complete orthonormal set of CSF's describing single and multiple excitations with respect to ψ_0. Then, the basic assumption is that the subspace M determining the M capture probability is spanned by the subset $\{\psi_i'\}$ whose members have "inner" configurations $1s^2 2s^2 3s$ or $1s^2 2s^2 3s^2$. Let N be the subspace spanned by the nondetected eigenstates $3s3p^6$ and $3d\ ^2S$, Φ the HF function for the initial state, and O the operator annihilating an electron at the nucleus; then the *measured M* capture probability P_M is the square of the projection of $O|\Phi\rangle$ onto $M \ominus N$, and can be summed by means of *any* basis set of $M \ominus N$. By CI calculation,[6] the subset $\{\psi_i''\}$ of $\{\psi_i'\}$ consisting of $\psi_0'' = 3s3p^6$, $\psi_1'' = 3d\ ^2S$, and the series $nd, \epsilon d\ ^2S$ $(n \geq 4)$ is transformed into an improved set $\{\Psi_j; j \geq 0\}$, Ψ_0 and Ψ_1 approaching the eigenstates $3s3p^6$ and $3d\ ^2S$, respectively. Then, we have (q_M neutrino energy)

$$P_M \sim q_M^2 \Big(\sum_{j\geq 2} |\langle \Psi_j | O | \Phi\rangle|^2 + \sum_s |\langle \psi_s' | O | \Phi \rangle|^2 \Big). \qquad (1)$$

The first term sums the transition probability to the correlation states, while the second sum extends over all ψ_s' not included in the CI calculation, and gives the transition probability due to the nonorthogonality between initial and final orbitals ("shakeoff"). Inserting $\Psi_j = \sum_i C_{ji} \psi_i''$ and $\sum_j |C_{ji}|^2 = 1$, evaluating the matrix elements, and applying closure to the "outer"[2] orbitals gives

$$P_M/P_L = (\lambda_M^0/\lambda_L^0)(B_M/B_L) \times [1 - (|C_{00}|^2 + |C_{10}|^2)F]. \qquad (2)$$

λ_M^0/λ_L^0 is the M/L ratio of the "usual" EC theory; B_i $(i = L, M)$, Bahcall's exchange, and $F \approx 0.85$, Vatai's overlap factor.[1] The squares of the mixing coefficients, somewhat dependent on an empirical scale factor, are $|C_{00}|^2 \approx 0.43-0.46$, $|C_{10}|^2 \approx 0.02-0.03$.[7] MCHF calculations[8,22] confirm $|C_{00}|^2$ on the whole (~ 0.50), but give no information about $|C_{10}|^2$. From (2), we obtain $P_M/P_L \approx 0.076-0.079$.

FSC does not alter the M-capture probability, but distributes it among final states. Chen and Crasemann[4] included final- and *initial*-state correlation (ISC) in a MCHF calculation, and found an 11% *reduction* of P_M/P_L with respect to Vatai's approach. As they sum over the final correlation states and neglect transitions due to the nonorthogonality of the initial and final orbitals, their result cannot be compared with experiment. It provides, however, an estimate of the error ($\sim$ 10%) introduced in the present analysis by disregarding ISC.[22]

Thus, the experimental result (0.073 ± 0.007) can be explained by FSC, and ISC can be disregarded in view of the present experimental and computational uncertainties. This agreement confirms the $3s3p^6$ assignment[20] and the summed $3s3p^6$ character of the two lowest ^2S states resulting from the CI calculation.[6]

Further experimental evidence for correlation in the Cl I $3s3p^6$ state comes from a low-energy satellite in L_{23} x ray[8] and $3s$ photoelectron spectra.[9-12] Comparison with EC is possible on the basis of the overlap approximation.[27] No correct designation of this satellite has been given so far. The usual assignment to $3d$, $4d$, and $4s\,^2S$ levels, by analogy to Ar II,[10-12,27] is ruled out in view of their positions relative to $3s3p^6$. Actually, the main satellite intensity is due to transitions to the $\epsilon d\,^2S$ continuum (correlation shakeoff), while correlation shakeup contributes only by a small percentage. Theory predicts approximately equal intensities for satellite and main peak[6,7]; in view of the high background in the photoelectron spectra and intense double-vacancy transitions contributing to the main L_{23} peak,[8,28] only qualitative agreement can be stated.

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