**Gas-Phase vs. Solution Energy Profiles.** The *unnormalized* solute distributions, $P_i(r_c)$, for the six windows are shown in Figure 5. Smooth Gaussian distributions with widths inversely proportional to the harmonic force constants, $k_i$, would be obtained if the true relative energy of the solution is exactly counterbalanced by the exponential term in the biasing potential (eq 9). This is roughly the case for windows 2–6, whose $P_i(r_c)$ are smooth distributions spanning increasing ranges of $r_c$. The distribution for the first window has two peaks, indicating that the variation in the pmf in this region is not perfectly compensated by the exponential biasing term. Nevertheless, the region from $r_c = 0$ to