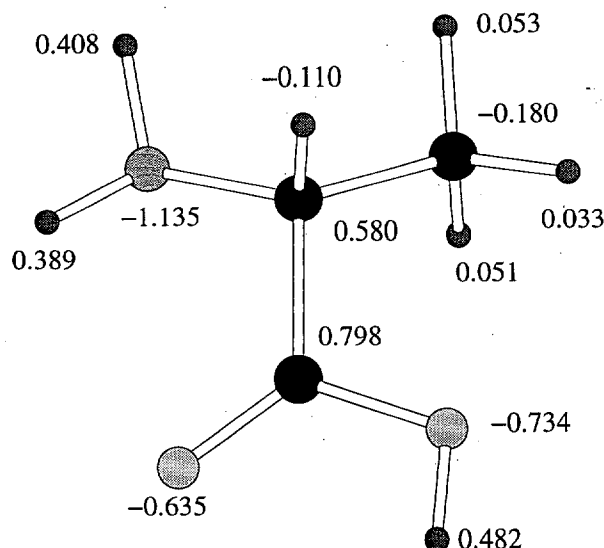
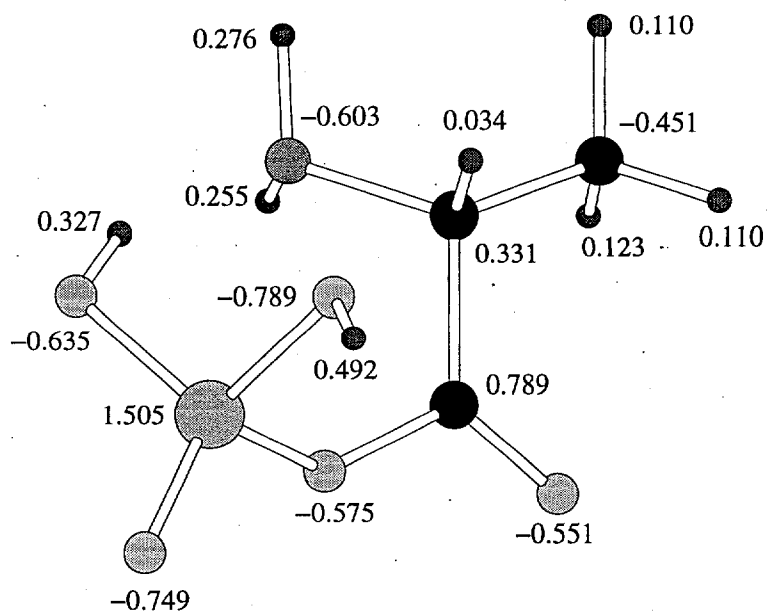


RHF/6-31+G* Structures and Partial Charges Used in the Study**Zwitterionic form of D-alanine**

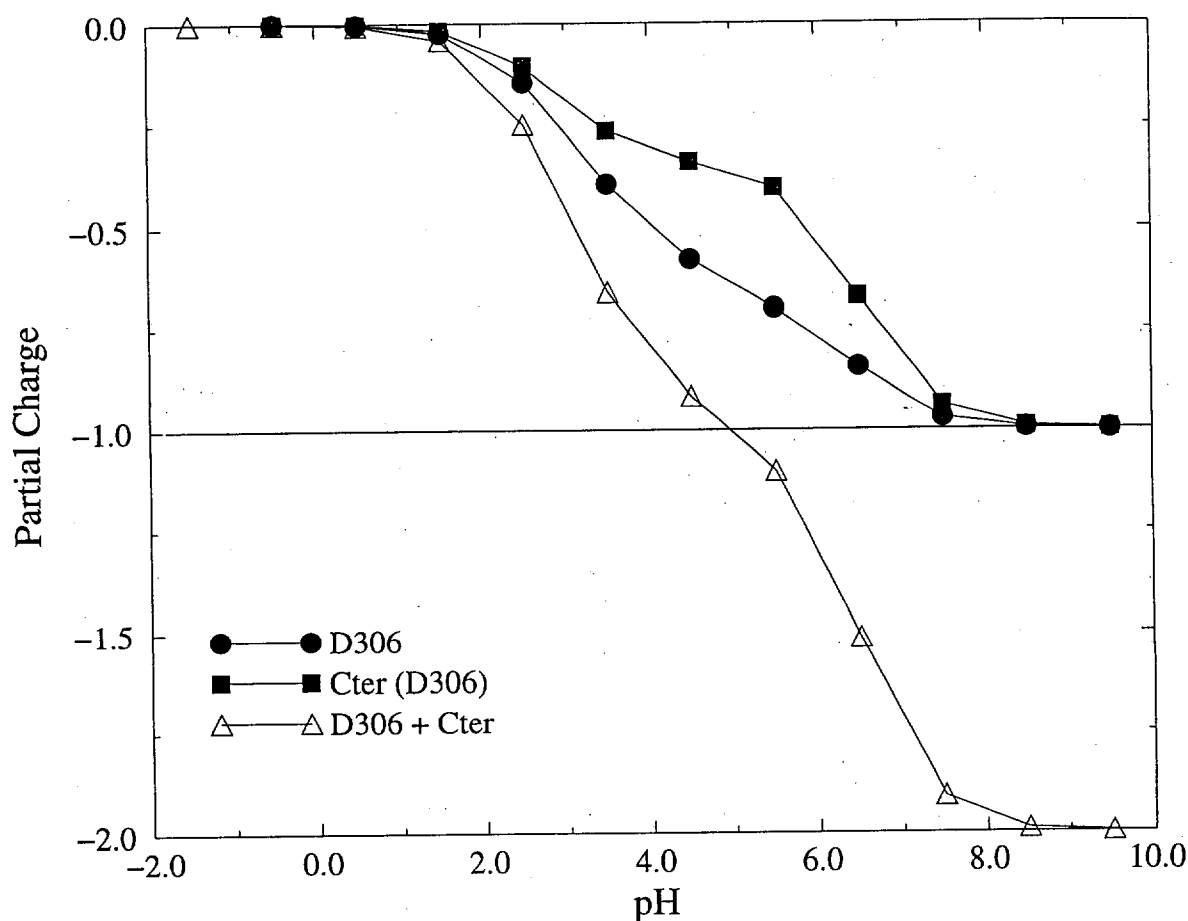
N	-0.927771	0.678685	-1.087191
C	0.274831	0.436376	-0.317961
C	0.260460	-1.001578	0.163995
O	-0.701659	-1.699921	0.194614
O	1.441647	-1.401828	0.622676
H	0.316608	1.024854	0.602577
C	1.510384	0.768205	-1.154546
H	2.422252	0.641182	-0.585711
H	1.549128	0.140412	-2.037253
H	1.453110	1.801050	-1.482680
H	1.353282	-2.290869	0.952905
H	-1.730723	0.258009	-0.663139
H	-1.096086	1.659539	-1.190714



Neutral form of the phosphoester derivative of D-alanine

N	-0.635444	1.567103	-1.805007
C	0.682655	1.138771	-1.327342
C	0.678737	-0.376918	-1.128757
O	1.501216	-1.090916	-1.574576
C	1.839823	1.567043	-2.223838
H	0.812647	1.573703	-0.343093
H	-0.675187	2.569219	-1.830669
H	-1.971279	0.991795	-0.585174
H	-0.796616	1.250323	-2.744512
H	1.750335	1.133549	-3.213430
H	1.841959	2.648489	-2.317282
H	2.790482	1.256619	-1.809824
O	-0.350882	-0.911021	-0.433529
P	-1.261881	-0.456010	0.806002
O	-2.318144	0.496233	0.170007
O	-1.775256	-1.563624	1.573979
O	-0.275245	0.488312	1.625935
H	-0.120670	0.164193	2.507134

Titration Curves of Asp306 and its C-terminus



As the C-terminus, D306 possesses two carboxylic acid functionalities with their central carbons only 3.05 Å apart. The close proximity and similar inherent acidities of these two groups creates a micro-system at the surface of the protein that allows for a shared proton. Both curves deviate more from the typical sigmoidal curve, black symbols. Adding the curves, open triangles (Δ), reveals a smooth double-transition. At pHs higher than 3.0, the first proton is lost from the side chain of D306. The side chain and the C-terminus share the second proton at what appears to be a 1:2 ratio, respectively. Both acids are deprotonated for pHs over 8. Though the form of the titration curves may seem unusual, they are not new. A previous study by Bashford and Gerwert involved very similar calculations to determine the pK_a s and titration curves of the ionizable sites within bacteriorhodopsin (*J. Mol. Biol.* **1992**, 224, 473-486). Similar titration characteristics with a range of cooperativity were seen for acidic side chains.