Ab initio study of the np (n=3-5) and 4s-3d Rydberg complexes of acetylene.

F. LARUELLE and J. LIEVIN
Laboratoire de Chimie Physique Moléculaire, Université Libre de Bruxelles, CPI 160/09, B-1050 Bruxelles, BELGIUM, .

Large scale internally-contracted MRCI calculations have been performed on the singlet states arising from the np (n=3-5) and 4s-3d Rydberg complexes of acetylene. Term energies are predicted with an accuracy of about 0.05 eV, leading to a reliable energy scale helpful for the interpretation of MPI spectra[a]. The Rydberg-valence and 4s-3d mixings are quantified from the analysis of the wave functions, and the corresponding anisotropy of the ionic core along the Rydberg series is discussed. Quantum defect values are reported. The calculations also investigate the region of the potential energy surfaces where the whole np series is crossed by doubly excited singlet valence states, namely by the $C'\ ^1A_g$ state [b]. This region corresponds to intermediate geometries between those of the linear ground state and of the trans bent C' state, i.e. around $R_{CC} = 1.4$ Åand $HCC = 140°$. The predissociative features of both the C' and the np Rydberg states are explained from the high degree of Rydberg valence mixing in this region.

[a] J.H. Fillion, A. Campos, J. Pedersen, N. Shafizadeh and D. Gauyacq, to be published.
[b] J. Liévin, J. Mol. Spectrosc. **156**, 123 (1992).