Nitrogen and Oxygen Catenation Projects

Structure and Properties of XN$_n$Y

Ab initio studies of the structure, vibrational frequencies, and intensities have been carried out on the open-chain species HN$_n$H, HN$_n$F, and FN$_n$F ($n=3,4$). Particular attention has been focused on the species HN$_3$H, which is isoelectronic with NO$_2$ and exhibits many of the same features in its electronic structure. HN$_3$H is shown to have a planar trans structure with $R$(N-N)=1.252 Angstroms, indicating considerable double-bond character. HN$_3$H also exhibits a low-lying doublet A$_2$ state separated from the ground state by about 36 kcal/mol. Replacement of one or more of the hydrogens in HN$_3$H by fluorines alters the electron distribution, spin density, and geometry, most importantly the NNN angle. The biradical species N$_4$ in its trans planar structure is shown to be of significantly higher energy than two N$_2$ molecules.

Structure and Properties of XO$_n$Y

Ab initio studies of the structure, vibrational frequencies, and intensities have been carried out on the open-chain species HO$_n$H, HO$_n$F, and FO$_n$F ($n=2,4$). Particular attention has been focused on the species HO$_2$F and HO$_3$H, which are isoelectronic. The former species has never been prepared experimentally but is of considerable interest as being intermediate between HO$_2$H and FO$_2$F which are both known but which have drastically different properties. As with most fluorine containing molecules a very high level calculation, at the QCISD level is needed. HO$_2$F behaves relatively normally in its bonding compared to FO$_2$F.

Structure and Properties of O$_n$

Ab initio studies of the structure, vibrational frequencies, and intensities have been carried out on the open-chain species O$_n$ ($n=2,5$). Particular attention has been focused on the species O$_5$, in both a cyclic and open-chain form. An equilibrium structure and vibrational frequencies have been obtained for O$_5$ in its lowest triplet state. Further calculations are in progress.