How Argon Atom Affects the Vibrational Structure of Protonated Nitrogen Dimers?

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The effect of the argon messenger atom in the vibrational spectra of protonated N_2 dimers are theoretically investigated. A multilevel potential energy surface (PES) and dipole moment function (DMF) are constructed and used for the anharmonic vibrational frequency calculations. The $Ar_mN_4H^+$ (m=0-1) underwent a geometry optimization and normal mode calculations at the CCSD/aug-cc-pVDZ level of theory. Both linear form and T-shaped ArN_4H^+ were found to be the possible structures for the argon-tagged protonated N_2 dimers. That is, the vibrational frequencies of linear ArN_4H^+ and T-shaped ArN_4H^+ are calculated to reproduce the experimental action protonated N_2 dimer spectrum. All ab initio calculations were performed using the Gaussian 09 suite of programs. Comparison of the calculated spectrum for the bare N_4H^+ ion and Ar-tagged N_4H^+ ion reveal that the reduction of the symmetry group, from $D_{\infty h}$ to either $C_{\infty v}$ or C_{2v}, results to a richer vibrational structure in the 500 – 1700 cm^{-1} region. When compared with the previously reported action spectra [1], it appears that both position isomers for ArN_4H^+ are needed to account for the additional bands in the observed spectrum. These findings demonstrate the active role of the messenger atom in relaxing some of the selection rules for the bare ion – resulting to an augmentation of the bands in the action spectrum.

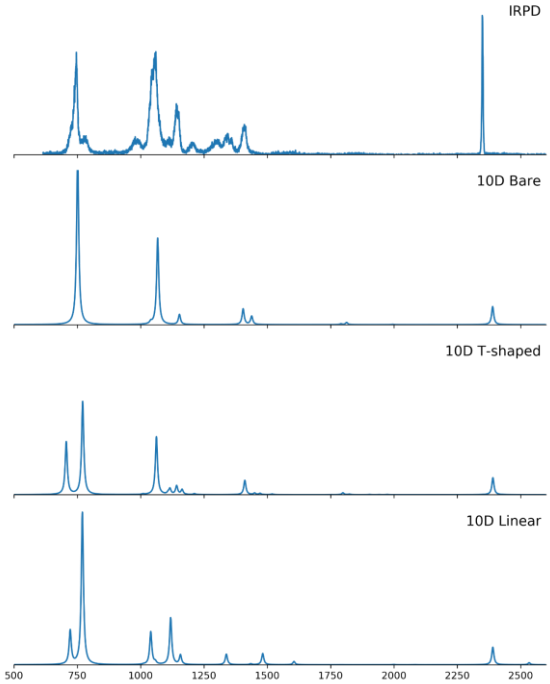

Figure 1: Infrared Photodissociation (IRPD) of ArN4H+ and calculated anharmonic spectrum for N_4H^+, ArN_4H^+ (T-shaped), and ArN_4H^+ (Linear).

References

1. A. M. Ricks, G. E. Douberly and M. A. Duncan, *J. Chem. Phys.*, **131** (2009), 104312.