

Second-Order Jahn-Teller Effect in Tetrahedral H_4X^{n+} ($n=0,1$; $X=O, S, Se, Te, Po$) - A Comparison with NH_4 and NH_4^-

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Highly protonated species are relevant in the design of materials for hydrogen storage and proton-exchange membranes. The existence of diprotonated hydrogen oxide and sulfide was postulated by Olah et al.[1] based on the observed hydrogen-deuterium exchange in “magic acids” and leading to various isotopologues of hydronium and sulfonium ions. The authors suggested that the D/H exchange occurs through the intermediacy of diprotonated species, H_4O^{2+} and H_4S^{2+} , and they computationally demonstrated the kinetic stability of these species.

The vertical electron affinity of H_4X^{2+} , approximately 13-14 eV, exceeds the first ionization potential of typical neutral molecules. Thus the reduction of the intermediate H_4X^{2+} to H_4X^+ is highly probable in typical chemical environments. A more recent and accurate electronic structure study (QCISD(T)/6-311G(2df,2p)) by Boldyrev and Simons[2] showed that reducing H_4X^{2+} with a single electron opens a dissociation channel to $H + H_3X^+$ with a significant energy release.

In this work we present an explanation for the origin of the instability of the H_4X^+ species, tracing it to a vibronic coupling between the ground 2A_1 and excited 2T_2 states leading to a negative curvature for one set of T_2 vibrational modes of H_4X^+ , which are dominated by XH stretches. We also characterize the second-order Jahn-Teller (SOJT) effect at the complete active space self-consistent field (CASCF) level using a formalism developed by Bearpark, Blancafort and Robb.[3] The local stability of H_4X^{2+} and the instability of H_4X^+ will be also illustrated for heavier chalcogens, Se, Te, and Po.

The geometric stability of the neutral tetrahedral radical NH_4 (2A_1) was predicted by Herzberg, [4] as if the vibronic coupling between the 2A_1 and excited 2T_2 electronic states was much

weaker than in the isoelectronic XH_4^+ (X =chalcogen) radicals discussed above. We shed light on this important difference analyzing again the vibronic couplings but also attempt more intuitive explanations, among them, the diffuse nature of the singly occupied orbital(SOMO).

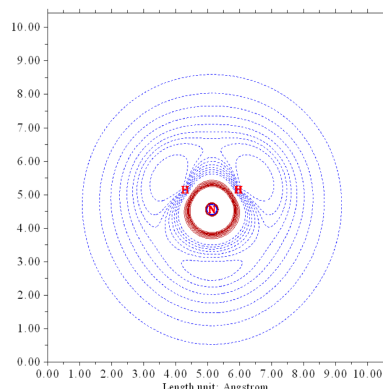


Figure 1: Contour plot of the SOMO orbital for NH_4 indicating its Rydberg character

Index Terms: potential energy surface, Jahn-Teller instability, dissociation dynamics

[1] Olah GA, et al, JACS, 108, 1986, 1032.

[2] Boldyrev AI, Simons J., JCP, 97, 1992, 4272.

[3] Bearpark MJ, Blancafort L, Robb MA., Mol. Phys., 100, 2002, 1735.

[4] Herzberg G., J Astrophys Astron, 5, 1984, 131.