

# VIBRATIONALLY AVERAGED STRUCTURE AND FREQUENCIES OF $(\text{XeHXe})^+$ : COMPUTATIONAL MOLECULAR SPECTROSCOPY STUDY

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We have proposed that the ro-vibrationally averaged structure of a linear molecule is observed as being “bent.”<sup>a</sup> To provide more evidence for this assertion, we here chose a linear molecule  $(\text{XeHXe})^+$ . We expected: The Xe atoms at both ends are so heavy that they stand still during vibration, so that in the bending mode, the central  $\text{H}^+$  atom inevitably moves perpendicularly against the  $a$  principal axis to give a “bent” ro-vibrationally averaged structure. The potential energy surface was calculated at the valence-CCSD(T)-DK3/[ANO-R3(Xe),cc-pV5Z-DK(H)] level, and ro-vibrational properties were calculated from the DVR3D wavefunctions in Discrete Variable Representation. The central  $\text{H}^+$ , which has  $+0.6 e$  charge, polarizes the Xe atoms by its reaction field, giving 136 kcal/mol of the heat of formation:  $(\text{XeHXe})^+$  is a stable cation. The equilibrium structure for  $\text{Xe1-H-Xe2}$  has  $r_e(\text{Xe1-H}) = r_e(\text{H-Xe2}) = 1.8694 \text{ \AA}$  and  $\angle(\text{Xe1-H-Xe2}) = 180^\circ$ , so that  $(\text{XeHXe})^+$  is a linear molecule. The ro-vibrationally averaged structure has  $\langle r(\text{Xe1-H}) \rangle_0 = 1.8913 \text{ \AA}$ ,  $\langle r(\text{H-Xe2}) \rangle_0 = 1.9017 \text{ \AA}$ , and  $\langle \angle(\text{Xe1-H-Xe2}) \rangle_0 = 166.6^\circ$ , indicating a large amplitude bending motion.

The harmonic vibrational frequencies  $\omega_1$  (antisymmetric stretch),  $\omega_2$  (bending), and  $\omega_3$  (symmetric stretch) are 824, 562, and  $149 \text{ cm}^{-1}$ , respectively. The corresponding term values  $\nu_1$ ,  $\nu_2$ , and  $\nu_3$  are 847, 545, and  $143 \text{ cm}^{-1}$ , respectively, to be compared with the values in *para*- $\text{H}_2$  matrix<sup>b</sup>  $\nu_1 = 847.0 \text{ cm}^{-1}$  and  $\nu_3 = 125.1 \text{ cm}^{-1}$ . The relation  $\nu_1 > \omega_1$  is a typical feature for [(ultra)heavy–light–(ultra)heavy] system. In the antisymmetric stretch mode, the central  $\text{H}^+$  moves back and forth between almost stand-still two Xe atoms just like a ball in catch-ball play, and hence the  $\nu_1$  value is not affected by matrix medium. On the other hand, the symmetric stretching mode should severely be affected by the mass of the matrix medium, as is reported,<sup>b</sup> since Xe atoms in this mode have to push out the cavity wall of the matrix.

<sup>a</sup>T. Hirano, U. Nagashima, P. Jensen, *J. Mol. Spectrosc.* **343**, 54 (2018); T. Hirano, U. Nagashima, M. Baba, *J. Mol. Spectrosc.* **369**, 111252 (2020); and references therein.

<sup>b</sup>M. Tsuge, J. Kalinowski, R.B. Gerber, Y-P. Lee, *J. Phys. Chem. A* **119**, 2651 (2015)