VIBRATIONALLY UNUSUAL BEHAVIORS PREDICTED FOR $(XeHXe)^+$: COMPUTATIONAL MOLECULAR SPECTROSCOPY STUDY

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We have reported on the vibrationally averaged structure and frequencies of $(XeHXe)^+$ at ISMS2021[a]: (a) $(XeHXe)^+$ is a linear molecule having a bent vibrationally averaged structure, (b) the ultra-heavy Xe atoms keep almost standstill during vibration, (c) severe matrix-effect for the ν_1 symmetric stretching mode, (d) $\nu_3 > \omega_{e,3}$ for the antisymmetric stretching mode, and (e) the zero-point structure has non-equivalent two r(Xe–H) bond distances irrespective of the potential being symmetrical for the bond-distance of these two bonds. We proposed in the previous report[a] that the unusual features (d) and (e) are characteristic for the [ultra-heavy]-[light]-[ultra-heavy] system. In this report, we disclose, from the viewpoint of computational molecular spectroscopy, why features (d) and (e) become characteristic for this system.

Based on the 3D vibrational potential energy surface (PES) calculated at the valence-CCSD(T)_DK3/[ANO-RCC 5ZP(Xe), cc-pV5Z-DK(H)] level, ro-vibrational wavefunctions (DVR3D wavefunction) were derived by the Discrete Variable Representation (DVR) method. In the antisymmetric stretching mode of a [ultra-heavy]-[light]-[ultra-heavy] system, the central light atom moves back and forth between the almost standstill ultra-heavy atoms just like a ball in catch-ball play. We will show this is the key for understanding unusual features (d) and (e), using the results of the PES and vibrational wavefunction analyses. We will also show why the symmetric stretching mode ν_1 is severely affected[b] by the molecular mass of the matrix medium.

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[a] T. Hirano, U. Nagashima, M. Baba, ISMS2021, WA07.

[b] M. Tsuge, J. Kalinowski, R.B. Gerber, Y-P. Lee, J. Phys. Chem. A **119**, 2651 (2015).