Electronic Supplementary information

Spectroscopic Evidence of S···N and S···O Hemibonds in the heterodimer cations

Xiaonan Sun,a Min Xie,*a Wei Qiu,a Chengcheng Wei,a Xujian Chen,a Yongjun Hu*a

AFFILIATIONS

a MOE Key Laboratory of Laser Life Science & Guangdong Provincial Key Laboratory of Laser Life Science, Guangzhou Key Laboratory of Spectral Analysis and Functional Probes, College of Biophotonics, South China Normal University, Guangzhou 510631, China

AUTHOR INFORMATION

*Corresponding Author

E-mail: xiemin@m.scnu.edu.cn (M.X.); yjhu@scnu.edu.cn (Y.J.H.)
Telephone: (+86-20) 8521-1920 EXT 8713. Fax: (+86-20) 8521-6052.
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Figure S1 The variation of infrared power in the range of 2400-3900 cm$^{-1}$. The black and blue curves show the variation of IR power with wavenumber at high and low IR power respectively. From 3440 cm$^{-1}$ to 3160 cm$^{-1}$, the infrared power increases as the wavenumber decreases. In the process of extending from 3160 cm$^{-1}$ to lower frequency, the infrared energy gradually weakens and approaches 0 mJ.
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Figure S3 Energy diagram of the VUV one-photon ionization of [CH$_3$SH-NH$_3$]$^+$ from the neutral ground state. The stable structures and transition state of the cationic [CH$_3$SH-NH$_3$]$^+$ and their relative energies (in kJ mol$^{-1}$) were calculated at the B3LYP-D3(BJ)/aug-cc-pVDZ level. “VIE” and “10.48 eV” represent the vertical ionization energy of each isomer and VUV photon energy respectively.
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Figure S9 Energy diagram of the VUV one-photon ionization of $[\text{CH}_3\text{OCH}_3\text{-H}_2\text{O}]^+$ from the neutral ground state. The stable structures and transition state of the cationic $[\text{CH}_3\text{OCH}_3\text{-H}_2\text{O}]^+$ and their relative energies (in kJ mol$^{-1}$) were calculated at the B3LYP-D3(BJ)/aug-cc-pVDZ level. “VIE” and “10.48 eV” represent the vertical ionization energy of each isomer and VUV photon energy respectively.