Supporting Information

Infrared photodissociation spectroscopic investigation on VO^+ and NbO^+ hydrolysis Catalyzed by Water Molecules

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The Supporting Information includes 14 pages with 27 figures.

Content

$VO(H_2O)_nAr^+$

$NbO(H_2O)_nAr^+$

$VO(H_2O)_nAr^+$

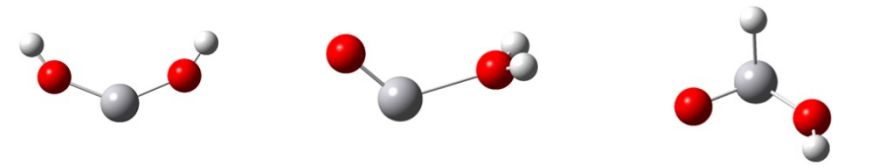

Fig. S1. Optimized structures of the minimum-energy isomers of $VO(H_2O)^+$. The relative energies (with ZPE correction) are given in kcal/mol.

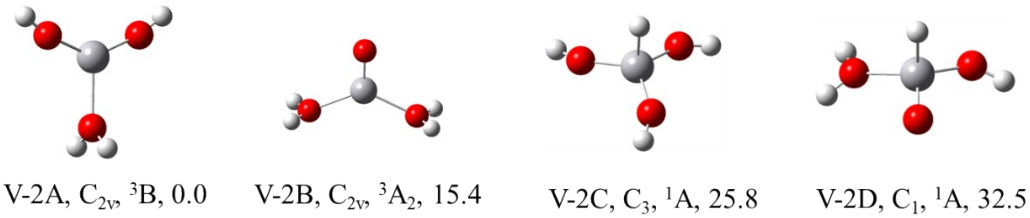

Fig. S2. Optimized structures of the minimum-energy isomers of $VO(H_2O)_2^+$. The relative energies (with ZPE correction) are given in kcal/mol.

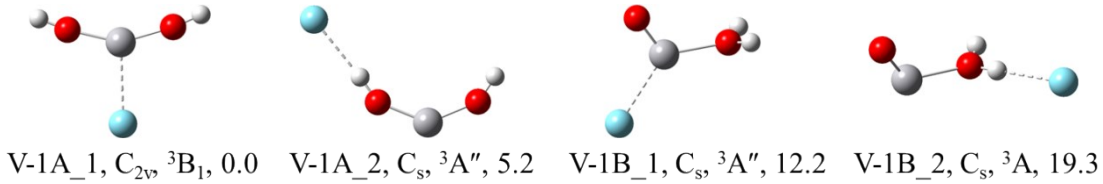

Fig. S3. Optimized structures of the minimum-energy isomers of $VO(H_2O)Ar^+$. The relative energies (with ZPE correction) are given in kcal/mol.

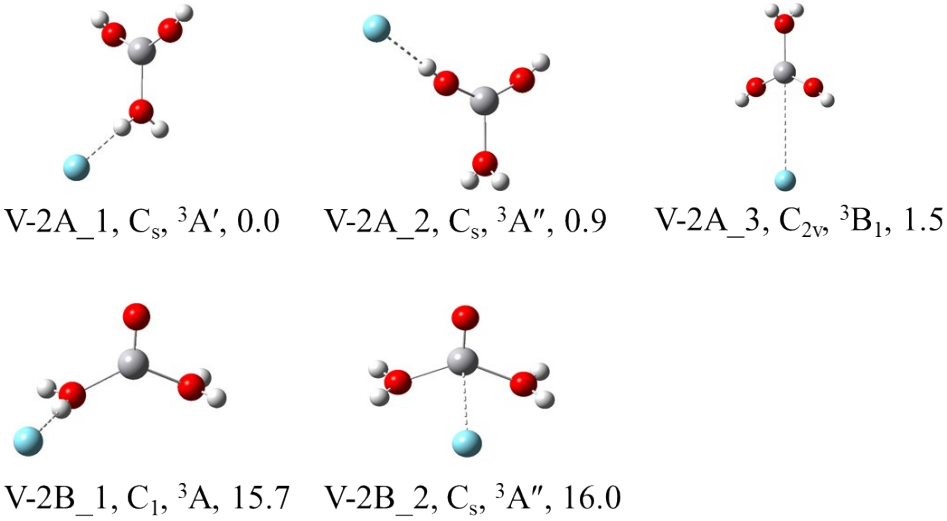

Fig. S4. Optimized structures of the minimum-energy isomers of $VO(H_2O)_2Ar^+$. The relative energies (with ZPE correction) are given in kcal/mol.

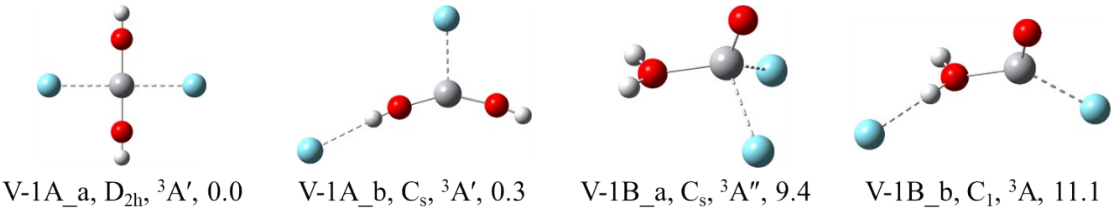

Fig. S5. Optimized structures of the minimum-energy isomers of $VO(H_2O)Ar_2^+$. The relative energies (with ZPE correction) are given in kcal/mol.

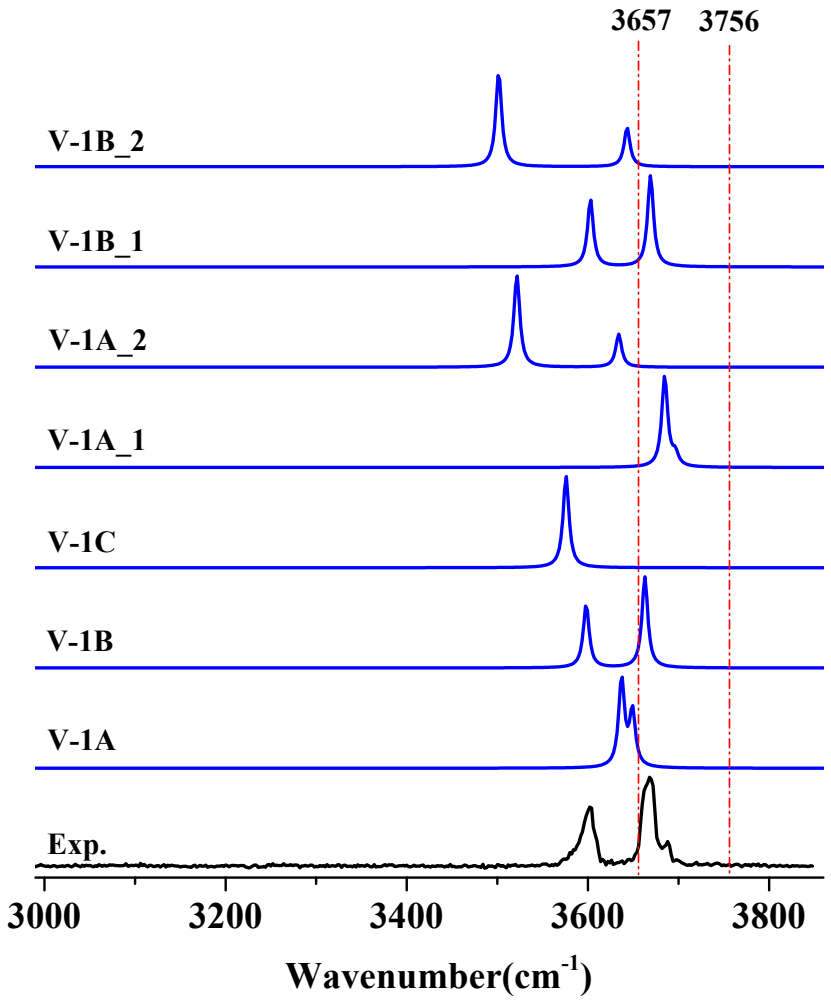

Fig. S6. Experimental infrared spectrum (black) and simulated vibrational spectra (blue) of $VO(H_2O)Ar^+$ in O-H stretching frequency region. The two dashed red lines are corresponding to the symmetric (3657cm^{-1}) and asymmetric (3756 cm^{-1}) stretches of the isolated water molecule.

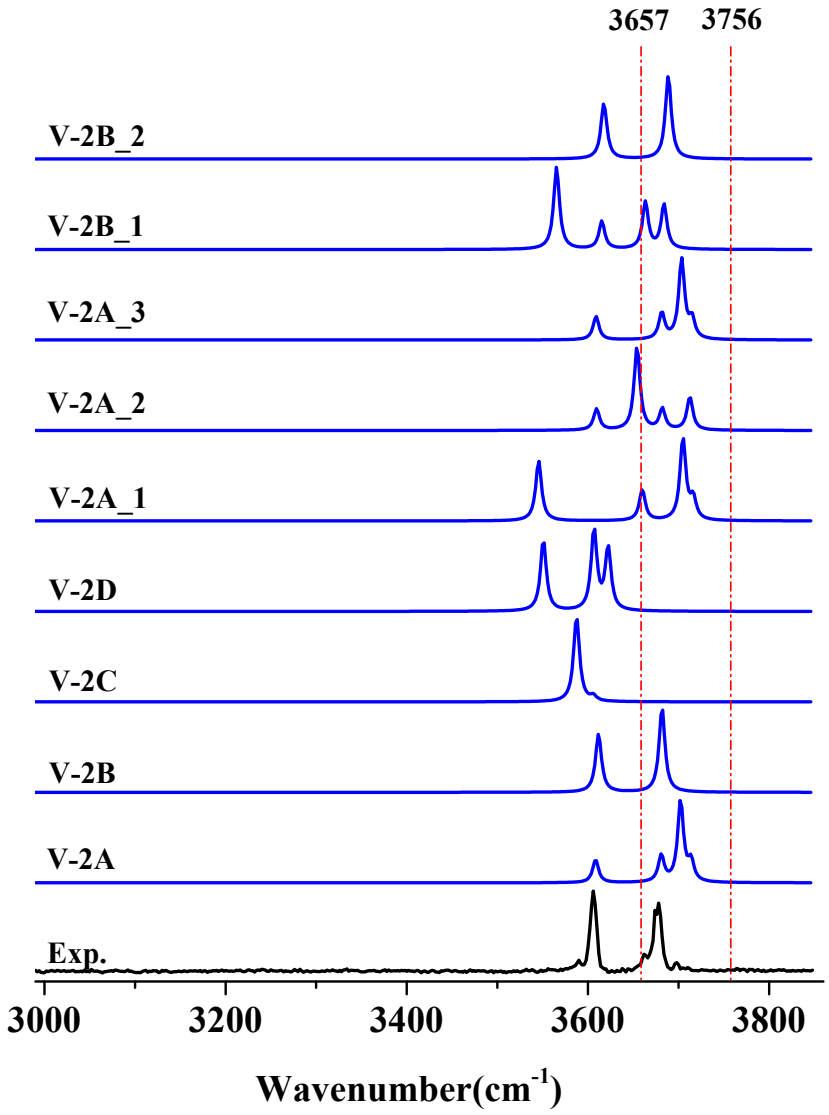

Fig. S7. Experimental infrared spectrum (black) and simulated vibrational spectra (blue) of $VO(H_2O)_2Ar^+$ in O-H stretching frequency region. The two dashed red lines are corresponding to the symmetric (3657cm^{-1}) and asymmetric (3756 cm^{-1}) stretches of the isolated water molecule.

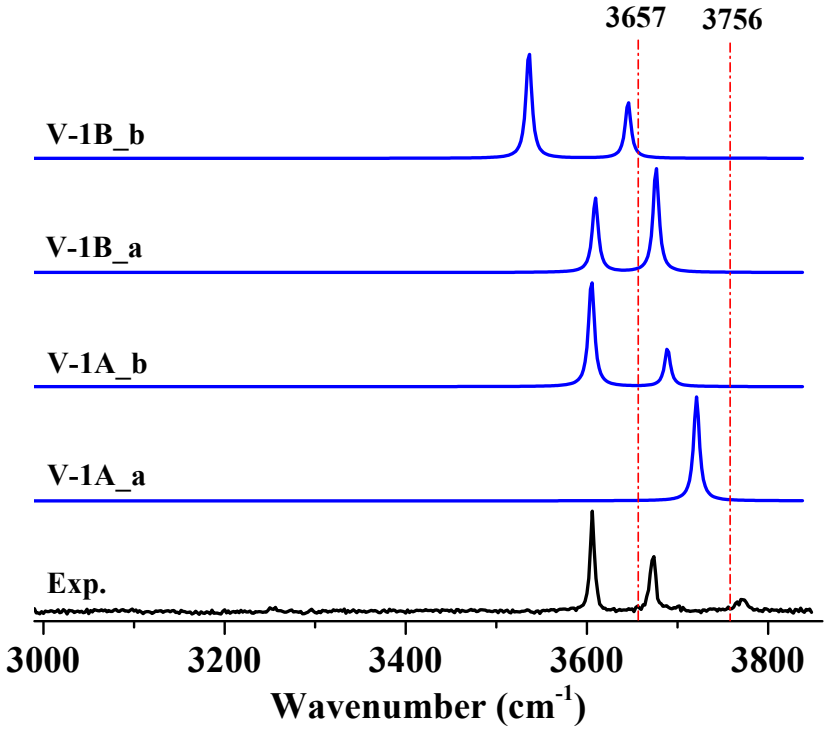

Fig. S8. Experimental infrared spectrum (black) and simulated vibrational spectra (blue) of $VO(H_2O)Ar_2^+$ in O-H stretching frequency region. The two dashed red lines are corresponding to the symmetric (3657cm^{-1}) and asymmetric (3756 cm^{-1}) stretches of the isolated water molecule.

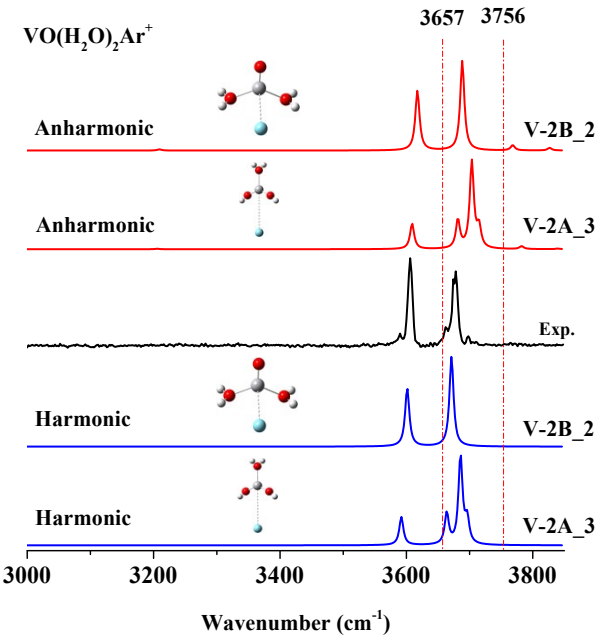

Fig. S9. Experimental infrared spectrum (black) of $VO(H_2O)_2Ar^+$, calculated anharmonic vibrational spectrum (red) and harmonic vibrational spectrum (blue) of V-2A_3 and V-2B_2 in O-H stretching frequency region. The two dashed red lines are corresponding to the symmetric (3657cm^{-1}) and asymmetric (3756 cm^{-1}) stretches of the isolated water molecule.

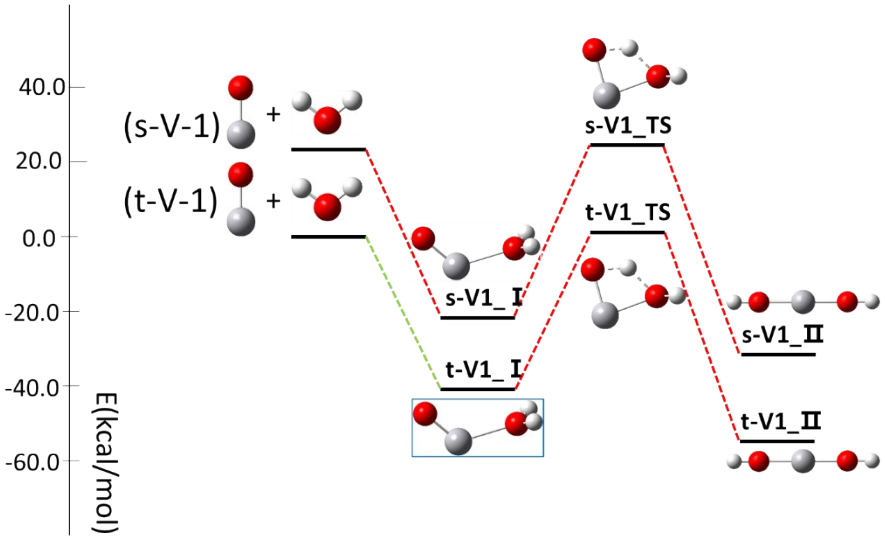

Fig. S10. Potential energy surfaces for the reactions of $VO^+ + H_2O \rightarrow VO(H_2O)^+$ (s-V-1: Singlet State; t-V-1: Triplet State).

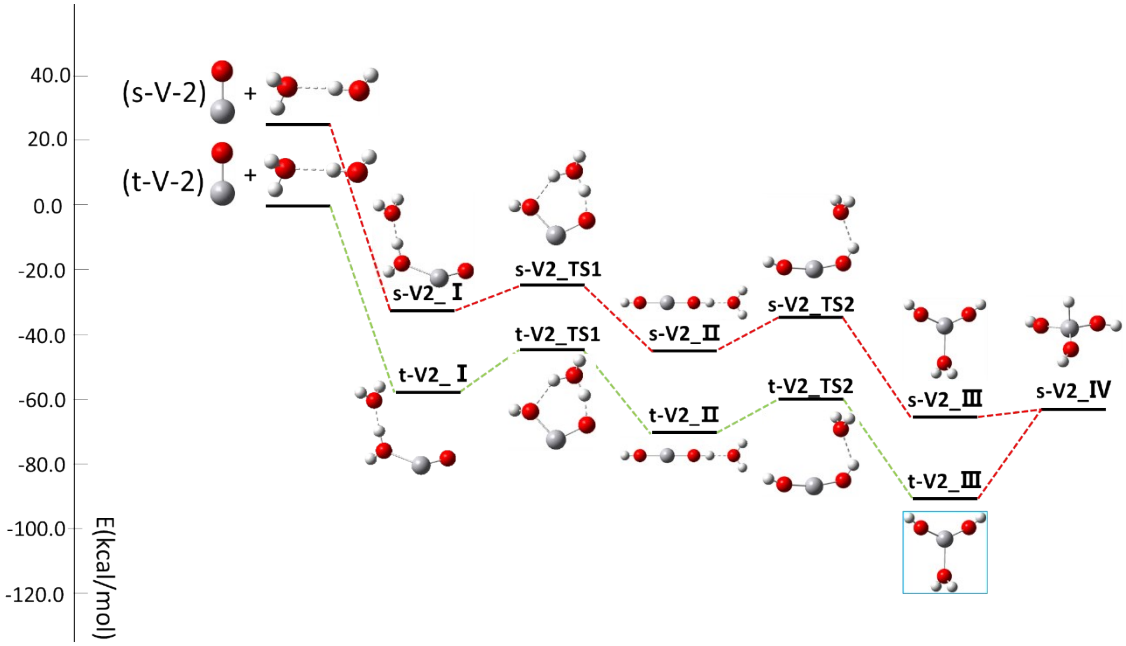

Fig. S11. Potential energy surfaces for the reactions of $VO^+ + 2H_2O \rightarrow V(OH)_2(H_2O)^+$ (s-V-2: Singlet State; t-V-2: Triplet State).

$NbO(H_2O)_nAr^+$

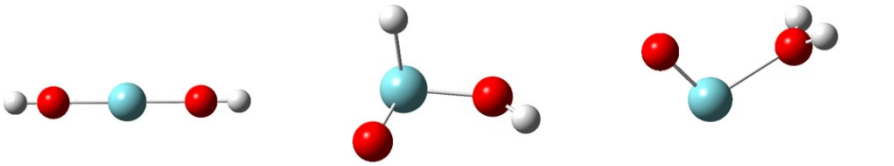

Fig. S12. Optimized structures of the minimum-energy isomers of $NbO(H_2O)^+$. The relative energies (with ZPE correction) are given in kcal/mol.

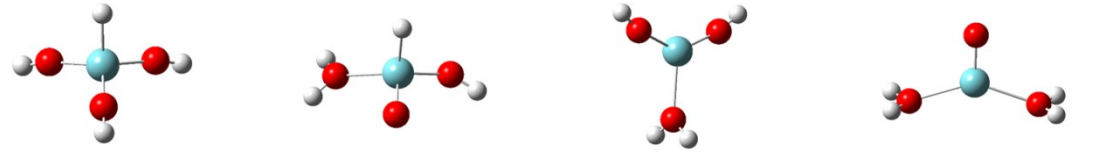

Fig. S13. Optimized structures of the minimum-energy isomers of $NbO(H_2O)_2^+$. The relative energies (with ZPE correction) are given in kcal/mol.

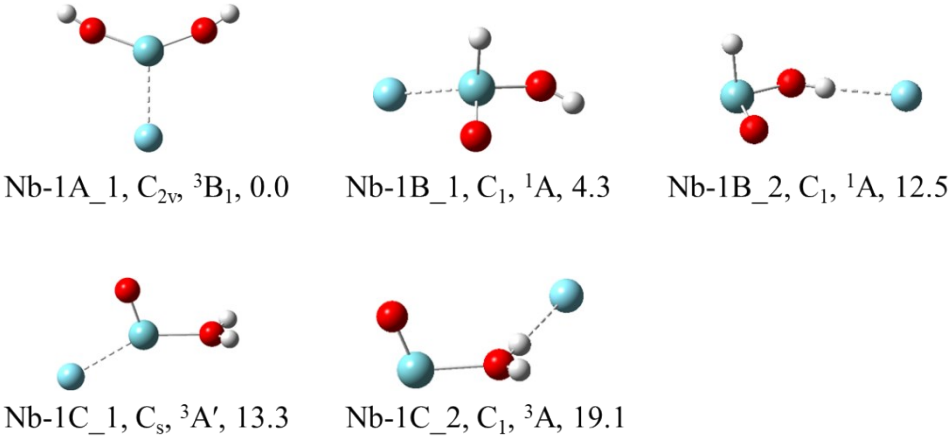

Fig. S14. Optimized structures of the minimum-energy isomers of $NbO(H_2O)Ar^+$. The relative energies (with ZPE correction) are given in kcal/mol.

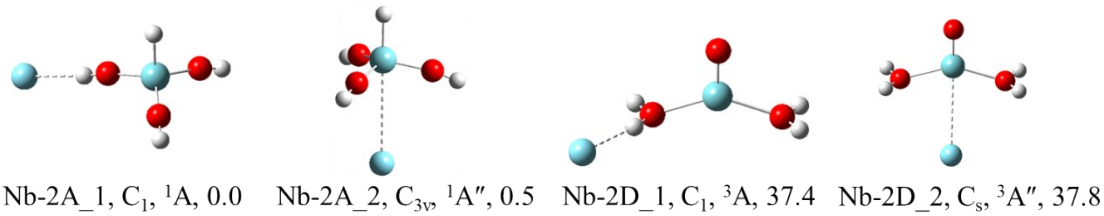

Fig. S15. Optimized structures of the minimum-energy isomers of $NbO(H_2O)_2Ar^+$. The relative energies (with ZPE correction) are given in kcal/mol.

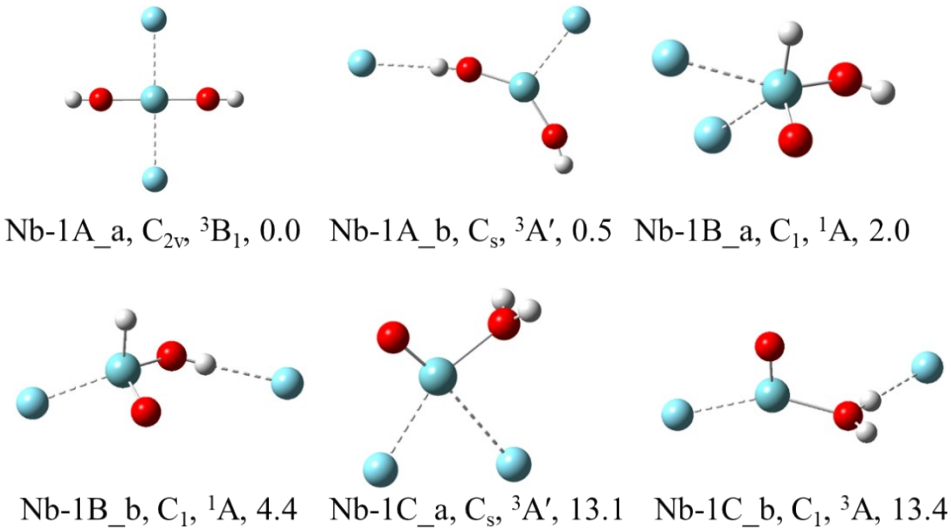

Fig. S16. Optimized structures of the minimum-energy isomers of $NbO(H_2O)Ar_2^+$. The relative energies (with ZPE correction) are given in kcal/mol.

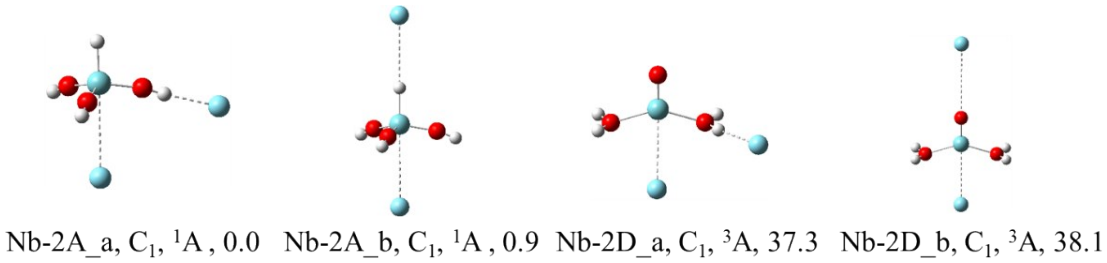

Fig. S17. Optimized structures of the minimum-energy isomers of $NbO(H_2O)_2Ar_2^+$. The relative energies (with ZPE correction) are given in kcal/mol.

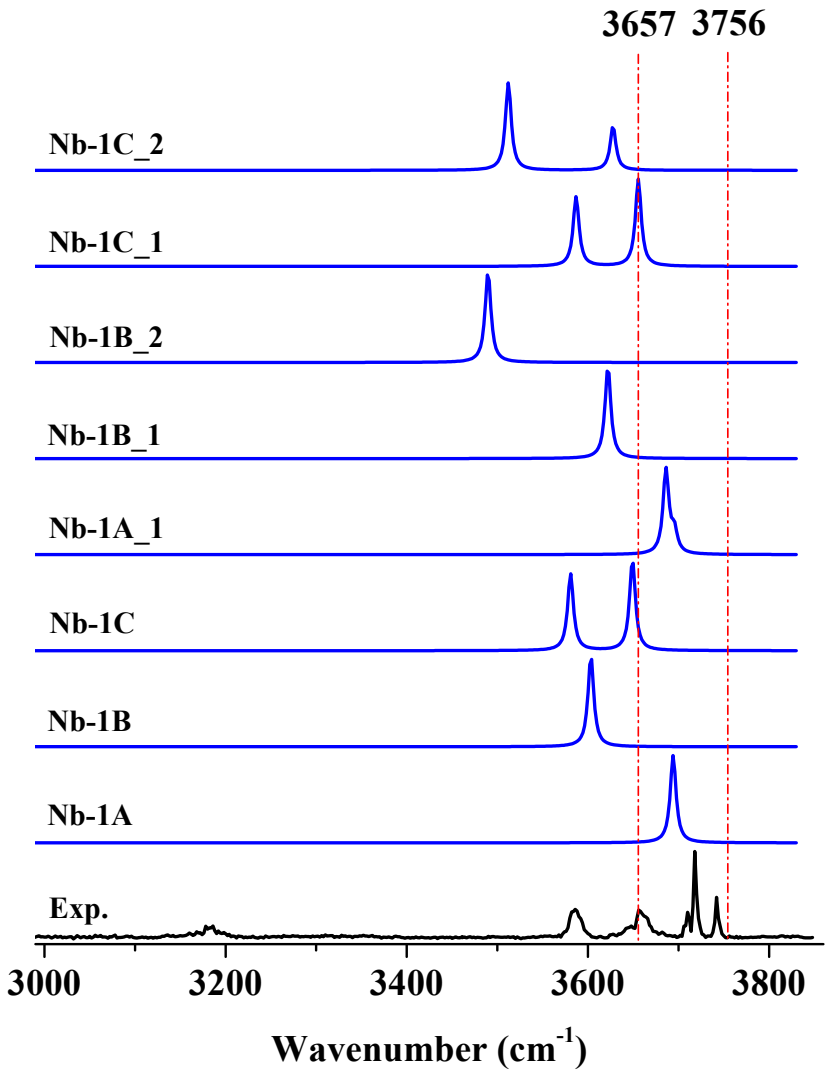

Fig. S18. Experimental infrared spectrum (black) and simulated vibrational spectra (blue) of $NbO(H_2O)Ar^+$ in O-H stretching frequency region. The two dashed red lines are corresponding to the symmetric (3657cm^{-1}) and asymmetric (3756 cm^{-1}) stretches of the isolated water molecule.

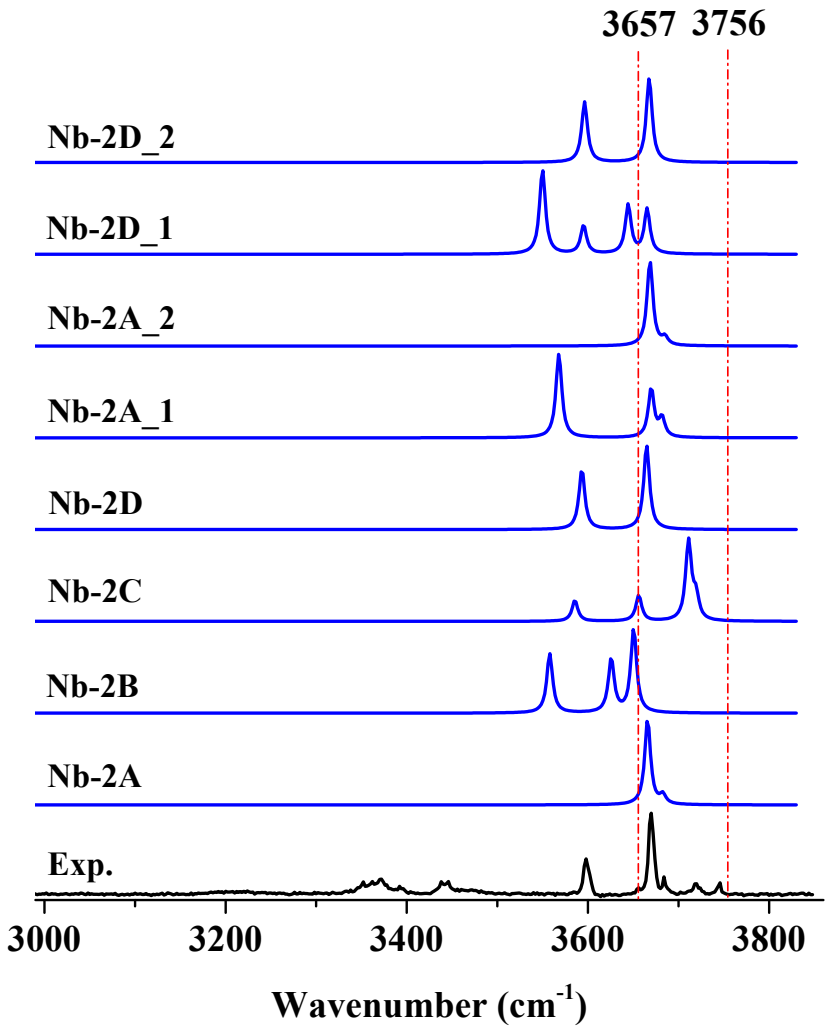

Fig. S19. Experimental infrared spectrum (black) and simulated vibrational spectra (blue) of $NbO(H_2O)_2Ar^+$ in O-H stretching frequency region. The two dashed red lines are corresponding to the symmetric (3657cm^{-1}) and asymmetric (3756 cm^{-1}) stretches of the isolated water molecule.

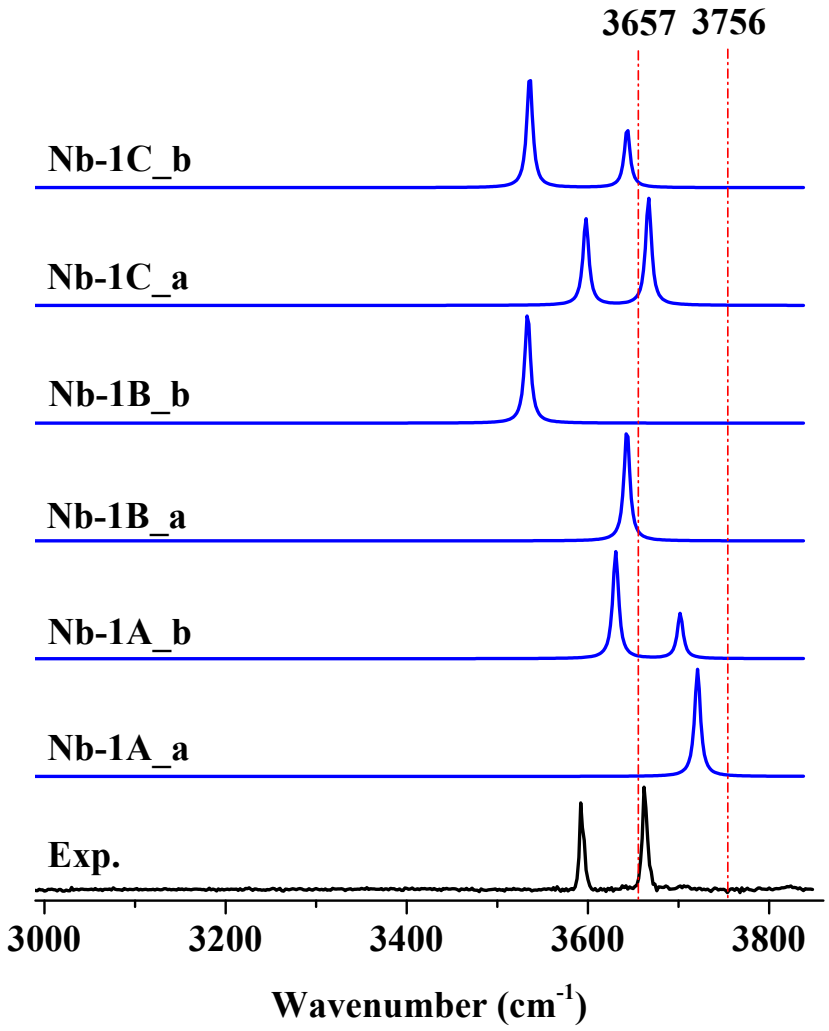

Fig. S20. Experimental infrared spectrum (black) and simulated vibrational spectra (blue) of $NbO(H_2O)Ar_2^+$ in O-H stretching frequency region. The two dashed red lines are corresponding to the symmetric (3657cm^{-1}) and asymmetric (3756 cm^{-1}) stretches of the isolated water molecule.

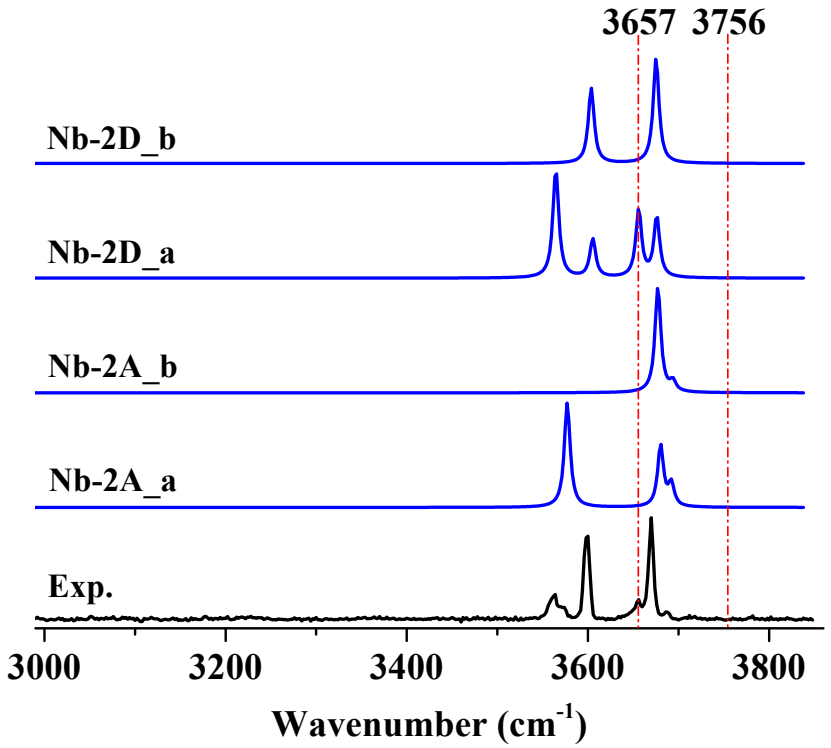

Fig. S21. Experimental infrared spectrum (black) and simulated vibrational spectra (blue) of $NbO(H_2O)_2Ar_2^+$ in O-H stretching frequency region. The two dashed red lines are corresponding to the symmetric (3657cm^{-1}) and asymmetric (3756 cm^{-1}) stretches of the isolated water molecule.

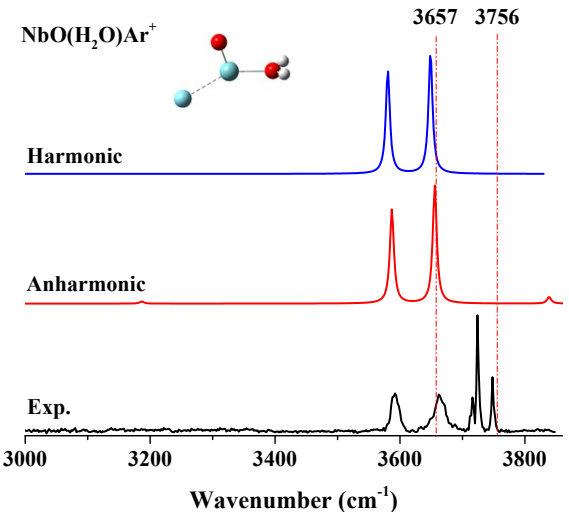

Fig. S22. Experimental infrared spectrum (black) of $NbO(H_2O)Ar^+$, calculated anharmonic vibrational spectrum (red) and harmonic vibrational spectrum (blue) of Nb-1C_1 in O-H stretching frequency region. The two dashed red lines are corresponding to the symmetric (3657cm^{-1}) and asymmetric (3756 cm^{-1}) stretches of the isolated water molecule.

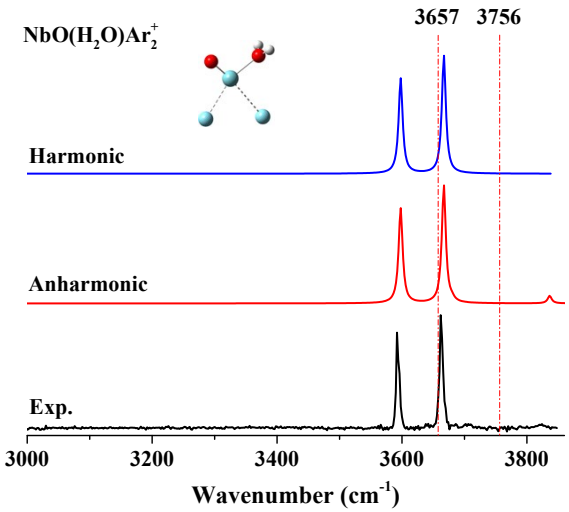

Fig. S23. Experimental infrared spectrum (black) of $NbO(H_2O)Ar_2^+$, calculated anharmonic vibrational spectrum (red) and harmonic vibrational spectrum (blue) of Nb-1C_a in O-H stretching frequency region. The two dashed red lines are corresponding to the symmetric (3657cm^{-1}) and asymmetric (3756 cm^{-1}) stretches of the isolated water molecule.

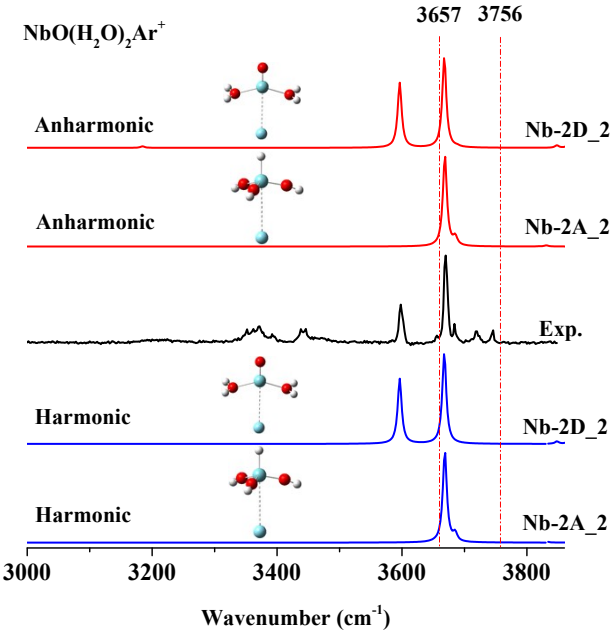

Fig. S24. Experimental infrared spectrum (black) of $NbO(H_2O)_2Ar^+$, calculated anharmonic vibrational spectrum (red) and harmonic vibrational spectrum (blue) of Nb-2A_2 and Nb-2D_2 in O-H stretching frequency region. The two dashed red lines are corresponding to the symmetric (3657cm^{-1}) and asymmetric (3756 cm^{-1}) stretches of the isolated water molecule.

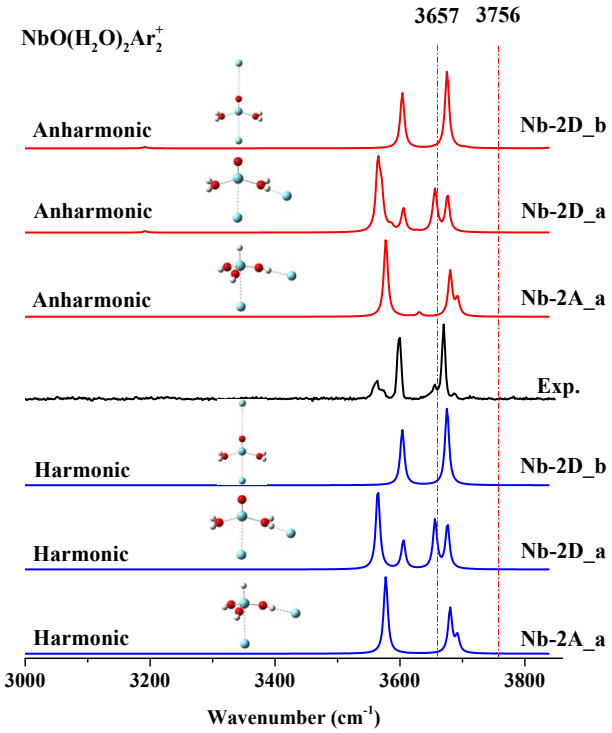

Fig. S25. Experimental infrared spectrum (black) of $NbO(H_2O)_2Ar_2^+$, calculated anharmonic vibrational spectrum (red) and harmonic vibrational spectrum (blue) of Nb-2A_a, Nb-2D_a and Nb-2D_b in O-H stretching frequency region. The two dashed red lines are corresponding to the symmetric (3657cm^{-1}) and asymmetric (3756 cm^{-1}) stretches of the isolated water molecule.

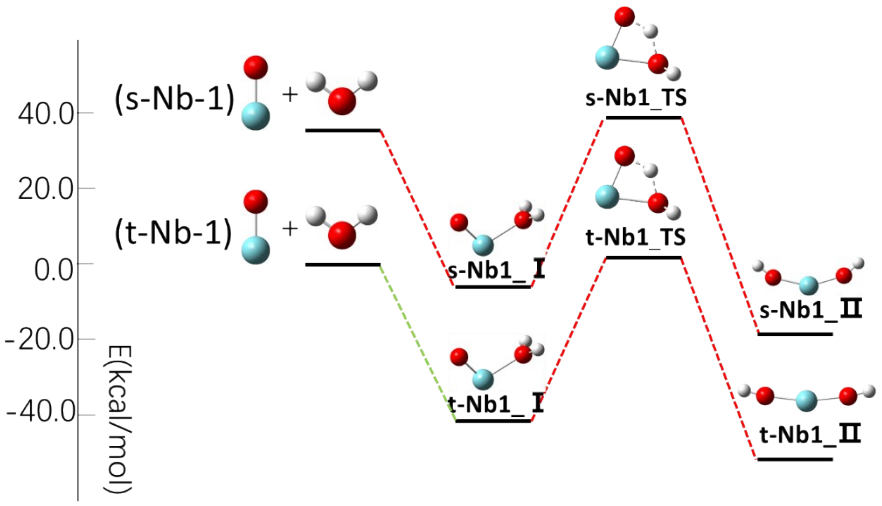

Fig. S26. Potential energy surfaces for the reactions of $NbO^+ + H_2O \rightarrow NbO(H_2O)^+$ (s-Nb-1: Singlet State; t-Nb-1: Triplet State).

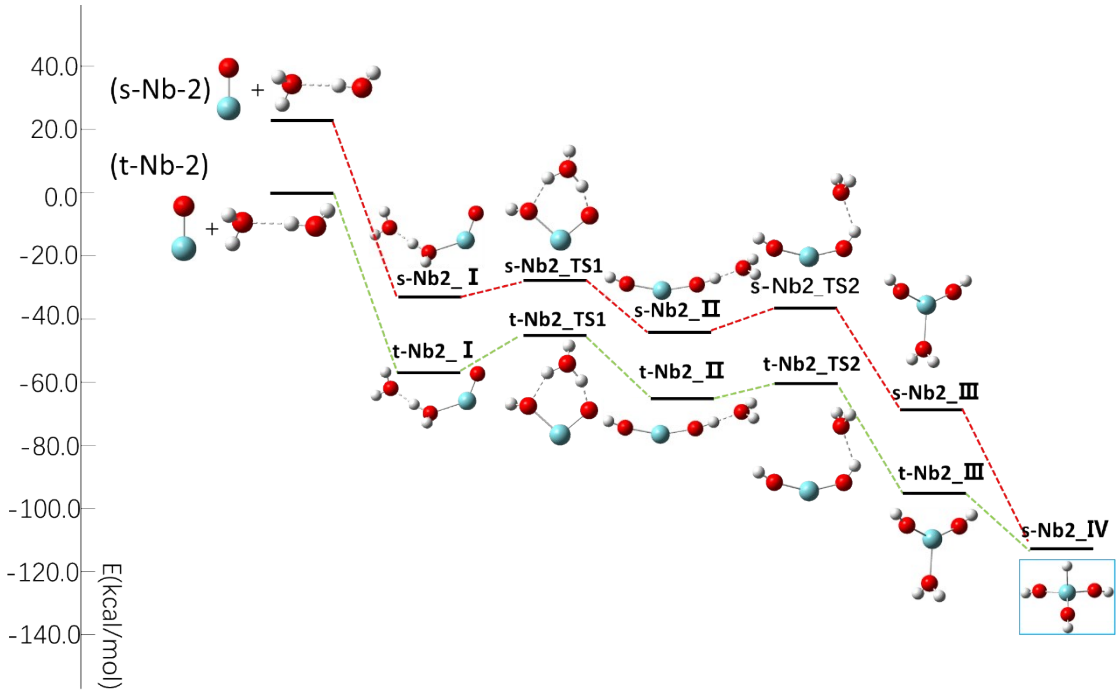

Fig. S27. Potential energy surfaces for the reactions of $NbO^+ + 2H_2O \rightarrow HNb(OH)_3^+$ (s-Nb-2: Singlet State; t-Nb-2: Triplet State).