

INFRARED SPECTRA OF THE OPEN SHELL IONIC COMPLEXES OH⁺-Rg (Rg=He,Ne)

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Mid-infrared spectra of the open shell ionic complexes OH⁺-Rg (Rg=He,Ne) have been recorded by photofragmentation spectroscopy in a tandem mass spectrometer^a. The ν_1 vibration (O-H stretch) and its combination band with the intermolecular bending vibration ($\nu_1+\nu_b$) have been observed for both complexes at the level of rotational resolution. The analysis of the spectra show that the dimers have linear proton-bound equilibrium structures in their $^3\Sigma^-$ electronic ground states with intermolecular center-of-mass separations of 2.60 and 2.65 Å, respectively. The fine structure of the ν_1 ($^3\Sigma^- \leftarrow ^3\Sigma^-$) and $\nu_1+\nu_b$ ($^3\Pi \leftarrow ^3\Sigma^-$) transitions arising from electron spin and vibrational angular momentum of ν_b have been analyzed in terms of a semi-rigid Hamiltonian including spin-spin, spin-rotation, and *l*-typing doubling interaction terms. The molecular parameters extracted from the obtained molecular constants provide valuable information on the radial and angular part of the intermolecular potential energy surface in each considered vibrational state.

^aD. Roth, S. A. Nizkorodov, J. P. Maier, and O. Dopfer, *J. Chem. Phys.* **109**, 3841, 1998.