HIGH RESOLUTION INFRARED SPECTRA OF AR-WATER AND NE-WATER AT 6 μm

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Ar- and Ne-water are highly floppy van der Waals complexes where the water subunit experiences nearly free internal rotation. Their ro-vibrational energy levels are characterized by the internal rotor states of the water subunit within the complex and a pseudo-diatomic rotational energy Hamiltonian. Large amplitude motions of the complexes lead to strong perturbations, such as Coriolis coupling and angular-radial coupling among the internal rotor states and the van der Waals bending and stretching states. Mid-infrared spectra of Ar- and Ne-water were measured with a direct absorption spectrometer with an external cavity quantum cascade laser at 6 μm and a 366-pass astigmatic absorption cell.[a] The scan-to-scan frequency instability of the laser was addressed with a "on-the-fly" calibration procedure. The infrared spectrum of Ar-water has been studied by Weida and Nesbitt,[b] in which the $\Sigma 1_{10}$ and $\Pi 1_{10}$ states have been identified. At least three new overlapping bands at 1630 cm^{-1} have been observed and two of them have been tentatively assigned to the $n = 1, \Sigma 1_{01} \leftarrow \Pi 1_{10}$ and $\Sigma 1_{10} \leftarrow \Sigma 1_{01}$ bands. The $n = 1, \Pi 1_{01} \leftarrow \Sigma 1_{01}$ band that was missing in the previous study was found at 1639 cm^{-1}. Four new bands in the 1645-1665 cm^{-1} region have been observed and assigned to the $\Pi 2_{12} \leftarrow \Pi 1_{01}$, $\Sigma 2_{12} \leftarrow \Sigma 1_{01}$, $\Pi 2_{12} \leftarrow \Sigma 1_{01}$, and $n = 1, \Sigma 1_{11} \leftarrow \Sigma 0_{00}$. A global fit of the microwave, far-infrared, near-infrared and mid-infrared data was performed with Pickett's SPFIT program to determine the spectroscopic constants of these levels. Infrared spectrum of Ne-water is analogous to that of Ar-water. The Ne-water PES[c] is much shallower than that Ar-water. As a result, there are fewer number of internal rotor states supported by the surface. Indeed, only the $\Pi 1_{10} \leftarrow \Sigma 1_{01}$, $\Sigma 1_{10} \leftarrow \Pi 1_{01}$, $n = 1, \Sigma 0_{00} \leftarrow \Sigma 0_{00}$, and $\Pi 1_{11} \leftarrow \Sigma 0_{00}$ bands were observed in our measurements. Severe spectral perturbations have been detected and analyzed. No infrared transitions of He-water were detected in the same frequency region. This is consistent with the previous theoretical calculation which predicted that the He-water potential supports only one bound state and no infrared transitions could be observed in this region because of the $b-$ type selection rule.

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[b] M. Weida, D. Nesbitt, *J. Chem. Phys.* **106**, 3078, 1997
[c] A. Haskopoulos, *J. Phys. Chem. A*, **114**, 8730, 2010