LEAK-OUT SPECTROSCOPY OF PROTONATED WATER DIMER I: RO-VIBRATIONAL SPECTRA

THOMAS SALOMON, OSKAR ASVANY, STEPHAN SCHLEMMER, *I. Physikalisches Institut, Universität zu Köln, Köln, Germany*.

The symmetric O-H stretching band of the protonated water dimer is re-investigated at high spectral resolution applying the novel action spectroscopic technique leak-out spectroscopy (LOS) in the 22-pole ion trap experiment COLtrap operated at 4 K. Ro-vibrational transitions of Helium buffer gas cooled $H_5O_2^+$ are excited using a narrow linewidth optical parametric oscillator prior to collisions with Neon as a second buffer gas. In doing so, part of the internal energy of the previously excited cation is transferred into kinetic energy (V-T-transfer) allowing it to surpass the electrostatic potential at the exit electrode of the 22-pole trap. The amount of cations exiting the trap time during the total trap time is monitored using a quadrupole mass-filter and a Daly-type ion detector. The resulting rotationally resolved spectrum is intrinsically background-free because the parent ground state ions are trapped without loss. The line intensities measured by LOS turn out to be closely related to the line intensities of conventional absorption spectroscopy. The new and extensive spectra are compared to previously presented high-resolution data obtained using a two-color-photodissociation scheme. Basically, the previously observed spectral complexity is confirmed by the novel action spectroscopic technique. The single-color leak-out spectra are more reliable in their actual line intensities as any impact on the dissociation efficiency originating from a variation of the optical overlap between two lasers experiments or power fluctuations are avoided. This improvement further simplifies the identification of Q-branches which can be nicely spotted in the high S/N spectra. Based on the multiplicity of these Q-branches and their separation, the tunneling motions at play for this molecular complex can be deciphered. Our findings challenge the current view on the struture and dynamics of the protonated water dimer.