Rotationally resolved Coherent Ion Dip Spectroscopy of high lying ground state van der Waals vibrations of the benzene · Ar complex

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Optical-optical double resonance experiments with intense, nearly Fourier transform limited nanosecond laser pulses are performed to investigate the electronic ground state (S_0) potential surface of benzene · Ar. To combine very high resolution and high sensitivity we apply the recently developed method of *Coherent Ion Dip Spectroscopy (CIS)* [a] [b] that is based on coherent light-matter interaction. The *CIS* method makes use of the special population dynamics in few level systems, interacting with two intense Fourier transform limited ns-laser pulses in special time sequences. Using a pulse sequence different from that of recent STIRAP population transfer experiments [c] we showed that a nearly 100% blocking of ionization is possible for double resonance conditions in aromatic molecules and molecular clusters. This leads to 100% deep ion dips.
New results for the S_0 ground state of the benzene·Ar complex are presented. Here, the high resolution of the *Coherent Ion Dip Spectroscopy* method allows the determination of very small isotope shifts of the van der Waals frequencies while the high sensitivity leads to the detection of hitherto not observed higher quanta of the van der Waals vibrations. In this way independent experimental data can be obtained to test theoretical calculations on mode mixing effects in the van der Waals potential without introducing additional free parameters into the calculations.
The isotope shifts for various van der Waals vibrations are compared to recent theoretical quantum mechanical 3D calculations of this model system performed by van der Avoird et al. .

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[b] R. Sußmann, R. Neuhauser, and H.J. Neusser, J. Chem. Phys. 103, 3315 (1995)
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