

THE INFRARED SPECTRUM OF THE BENZENE CATION

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The Infrared (IR) absorption spectrum of the Jahn-Teller distorted benzene cation has been recorded using IR photodissociation. In this method, benzene–rare gas atom Van der Waals complexes are formed in a molecular beam and resonantly ionized, yielding vibrationally cold complex cations. The complexes are subsequently irradiated by IR light of the free electron laser FELIX and detected in a time-of-flight mass spectrometer. The frequency of FELIX is scanned over a large region (250-1700 and 2800-3200 cm^{-1}). Upon hitting a vibrational resonance the complex can dissociate and by monitoring the ion current of fragment ions as a function of the IR frequency the IR spectrum is recorded.

A detailed comparison between the IR absorption spectra of benzene-Ne and benzene-Ar in selected spectral regions shows that the spectrum of the benzene-Ne cation indeed represents the IR absorption spectrum of the bare benzene cation. When using Ne as a messenger atom in the IR photodissociation technique, Van der Waals sidebands can appear in the spectrum, but no effects of the formal symmetry breaking in the complex due to the presence of the messenger atom have been observed.

Based on this evidence we conclude that the IR photodissociation spectrum of the benzene-Ne complex cation is the true and complete IR spectrum of the benzene cation, and should serve as a benchmark for future analyses of the vibrational properties of this important species.