

VISIBLE PHOTODISSOCIATION SPECTRA OF THE 1-METHYL AND 2-METHYLNAPHTHALENE CATIONS: LASER SPECTROSCOPY AND THEORETICAL SIMULATIONS

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Naphthalene (Np) and its methylated derivatives (1-Me-Np and 2-Me-Np) are prototype molecules for spectroscopists as first members of the polycyclic aromatic hydrocarbons (PAHs) family. High resolution studies are capable to explore the details of the internal rotation of the methyl group. Although this was achieved in neutral PAHs^b, the task is not the same in cations. Me-Np cations have been probed by resonance-enhanced multiphoton dissociation^c, showing only very broad and unresolved spectra, while absorption in argon matrix revealed more resolved vibronic bands^d.

The electronic absorption gas phase spectra of 1-Me-Np⁺ and 2-Me-Np⁺ were measured using an Ar-tagging technique. In both cases, a band system was observed in the visible range and assigned to the $D_2 \leftarrow D_0$ transition. The 1-Me-Np⁺ absorption bands revealed a red shift of 808 cm⁻¹, relative to Np⁺ (14 906 cm⁻¹)^e, while for 2-Me-Np⁺ a blue shift of 226 cm⁻¹ was found. A short vibrational progression was also observed. Moreover, insights into the internal rotation motion of the CH₃ were inferred, although intrinsic broadening due to intramolecular relaxation was present. These measurements were supported by detailed quantum chemical calculations that allowed exploration of the potential energy curves, along with a complete simulation of the harmonic FC factors using the cumulant Gaussian fluctuations formalism, extended to include the internal rotation.

^apresently at University of Marseille (PIIM), France

^bsee for instance Baba et al, *J.Phys.Chem.A*, **2009**, 113, 2366

^cDunbar et al, *J. Am. Chem. Soc.* **1976**, 98, 7994-7999 and *J.Phys.Chem.* **1985**, 89, 3617

^dAndrews et al, *J.Phys.Chem.* **1982**, 86, 2916

^ePino et al, *J. Chem. Phys.* **1999**, 111, 7337-7347