ISOMER-SPECIFIC INFRARED SPECTROSCOPY AS A DIAGNOSTIC TOOL FOR REACTIVE INTERMEDIATES TOWARDS NAPHTHALENE

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In the context of combustion, both the formation and destruction of fused-ring aromatics are important to understand in some detail. Determining the principal pathways from benzene to naphthalene and on to larger polyaromatic hydrocarbons is imperative, but with increased chemical complexity is likely to involve free radicals as intermediates which are themselves structurally complex, necessitating more detailed spectroscopic characterization for their identification. Our group has recently studied the vibronic spectroscopy of a series of $C_{10}H_9$ and $C_{10}H_{11}$ hydronaphthyl radicals, in which their thermochemical properties were evaluated with isomer specificity.[a] Here, we extend this characterization to include infrared spectra in the alkyl CH stretch region, and explore the spectroscopic consequences of electronic excitation on these CH stretch absorptions. Utilizing resonant ion-dip infrared spectroscopy (RIDIRS), we report the infrared spectra of 2,3,4-Trihydronaphthyl ($C_{10}H_{11}$) and Inden-2-ylmethyl ($C_{10}H_9$) radicals taken in the alkyl and aromatic CH stretch regions. The latter radical was misidentified in earlier studies by our group[a] as 2-Hydronaphthyl radical, appearing in a discharge of 1,2-Dihydronaphthalene in close proximity to 1-Hydronaphthyl radical. The alkyl CH stretch IR spectrum positively identifies the radical as Inden-2-ylmethyl radical, as recently reported by Schmidt and co-workers.[b] RIDIR spectra in the D_1 excited state will also be reported. These spectra show significant changes that reflect the response of the CH stretch absorptions to electronic excitation. The implications of such measurements for future studies of free radicals will be discussed.

[a] J. A. Sebree, V. V. Kislov, A. M. Mebel, and T. S. Zwier *J. Phys. Chem. A* **114** (6255-6262), 2010.

[b] T. P. Troy, N. Chalyavi, A. S. Menon, G. D. O'Connor, B. Fückel, K. Nauta, L. Radom, and T. W. Schmidt *Chem. Sci.* **2** (1755-1765), 2011.