DIRECT-ABSORPTION OBSERVATION OF A DOUBLY-FORBIDDEN ELECTRONIC TRANSITION IN DIACETYLENE USING CAVITY RING-DOWN SPECTROSCOPY

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The nominally $^3\Delta_u \leftarrow X^1\sigma_g^+$ transition in room-temperature diacetylene has been observed by direct absorption for the first time using the cavity ring-down technique pioneered by O'Keefe and Deacon [a]. Using mirrors with high reflectivity (99.85%) the wavelength range 396 nm - 342 nm was investigated. Two bands at 27090 cm^{-1} and 27430 cm^{-1} are observed which show a red shading consistent with a $\pi^* \leftarrow \pi$ transition. Band contours also suggest a linear to bent electronic excitation. The largest spectral feature has a measured molar absorption coefficient of $1.5\text{x}10^{-4} Lmol^{-1}cm^{-1}$. The $^3\Delta_u$ state is one of the states thought to be responsible for photochemical reactivity.

[a] A. O'Keefe and D. A. G. Deacon, Rev. Sci. Instrum. 59, 2544 (1988).