LASER EXCITED METASTABLE SPECTROSCOPY OF C_2H_2

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Triplet states have been detected near the $3\nu_3$ vibrational level of the S_1 electronic surface of C_2H_2 using the highly selective technique of Laser Excited Metastable (LEM) spectroscopy. LEM detects metastable molecules through the detection of an Auger electron emitted when the molecule impacts a metal surface. A supersonic molecular beam of C_2H_2 was crossed with a laser beam which excites $\pi^* - \pi$ transitions to metastable states. The molecules then travel $\sim$100 μs before impacting a Au surface. During the collision, an electron from the conduction band of the metal may fall into the open π bonding orbital of C_2H_2. The electron in the π^* orbital is then ejected and detected. To be detected, the excited state must have a minimum lifetime on the order of 100 μs and must have electronic excitation energy that exceeds the work function of the Au surface ($\phi = 5.1$ eV). The LEM and LIF spectra were recorded simultaneously for a number of bands in the $\tilde{A}$-$\tilde{X}$ band system, including $3\nu_3$. LEM and LIF offer complementary information. LIF detects short-lived states which are of predominant singlet character; LEM detects long-lived states which are predominantly triplet. The spectra show a number of interesting features necessary to understanding the mechanism of singlet-triplet coupling in C_2H_2. Despite the low vibrational density of T_3 states near $3\nu_3$, the results show that a single vibrational level of the T_3 surface is strongly coupled to $3\nu_3$ and to the much denser manifold of T_1 and T_2 vibrational states.