PURE ROTATIONAL SPECTROSCOPY AS A PROBE OF PHOTODISSOCIATION DYNAMICS

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Many probes of photodissociation dynamics, such as laser induced fluorescence (LIF), resonance enhanced multiphoton ionization (REMPI), or time-resolved Fourier transform infrared absorption (TR-FTIR), suffer from spectral congestion and an enormous spectroscopic burden to convert observable transition strengths into populations. Pure rotational spectroscopy, however, does not suffer from these problems because the high resolution and the dependence of the rotational constant on vibrational level assure that rotational lines of different vibrational levels are well resolved. Moreover, population measurements are simplified because the permanent electric dipole moment can be accurately calculated or measured for each species or vibrational state. Despite the quantitative, species-selective, and nearly universal properties of rotational spectroscopy, it is seldom used as a probe of photodissociation dynamics. Here, we demonstrate that millimeter-wave spectroscopy is capable of measuring vibrational distributions and branching ratios of photolytic products. The technique is applied to the photolysis of acrylonitrile at 193 nm to measure the branching ratio of the HCN and HNC products.