VIBRATIONAL POPULATION DISTRIBUTION IN FORMALDEHYDE EXPANDING FROM CHEN PYROLYSIS NOZZLE MEASURED BY CHIRPED PULSE MILLIMETER WAVE SPECTROSCOPY

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Knowing the vibrational population distribution of unimolecular fragmentation reaction products can reveal the reaction mechanism. Here, we applied Chirped Pulse Millimeter Wave (CPmmW) spectroscopy, invented by Brooks Pate and co-workers [a], to detect the vibrational population distribution of formaldehyde produced by pyrolysis of methyl nitrite (CH_3ONO) or ethyl nitrite (CH_3CH_2ONO). The pure rotational spectrum contains information about vibrational populations via the known vibration dependence of the rotational constants, which is easily observed in the millimeter-wave spectrum. Only two of six vibrational modes of formaldehyde are significantly populated in both pyrolysis decomposition reactions and in an expansion of pure formaldehyde, suggesting that it is the collisional energy transfer that primarily determines the vibrational population distribution. The non-Boltzmann population distribution among the observed vibrational modes demonstrates non-statistical vibrational energy transfer in formaldehyde. It is in sharp contrast with the equilibrated population distribution measured in OCS and the almost complete vibrational relaxation observed in acetaldehyde.
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[a] G. G. Brown, B. C. Dian, K. O. Douglass, S. M. Geyer, S. T. Shipman and B. H. Pate *Rev. Sci. Instrum.* **79**, 053103 (1995).