

SIGNATURES OF PHOTODISSOCIATION MECHANISM OF *SYMMETRIC*-TRIAZINE ENCODED IN THE VIBRATIONAL POPULATION DISTRIBUTION OF HCN PHOTOFRAGMENTS USING 266 NM

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We present photodissociation reaction dynamics utilizing *rotationally-resolved* Chirped-Pulse Fourier Transform Millimeter-Wave (CP-FTmmW) spectroscopy. The *state-specific vibrational population distribution* (VPD) of the photofragments contains mechanistic details of the reaction. VPD obtained from our experiments is complementary to dynamics experiments that measure the kinetic energy distributions of the photofragments. This complementarity to previous classic experiments yields tantalizing insights.

We study photodissociation dynamics of 1,3,5-Triazine (*symmetric*-Triazine) to form 3 HCN molecules in a seeded supersonic jet using 266 nm radiation. The vibrational cooling *inefficiency* in the jet preserves the VPD of the photofragments, while rotational cooling enhances the signal of low-J pure-rotational transitions. The multiplexed nature of the spectrometer enables *simultaneous sampling* of several ‘vibrational satellite transitions’ that belong to different vibrational states but the same (J+1)-J rotational transition, in this case the J:1-0 transition of HCN. With at least 3.2% vibrational excitation among the photofragments, we observe a higher excitation in the bending vibrational mode of HCN (up to $\nu_2=6$) than in the CN stretching mode (up to $\nu_3=2$); no C-H stretching (ν_1) excitation was observed, nor was any HNC isomer population detected. The observed VPD along the even- ν states of ν_2 vibrational progression is at least bimodal, implying an *asymmetric* partitioning of vibrational energy among the HCN photofragments. This signature in the HCN VPD indicates a *sequential* dissociation mechanism of *symmetric*-Triazine initiated by 266 nm radiation.

Since VPDs are mode-specific, the *adiabatic* Franck-Condon projection onto the vibrational modes is capable of providing *local structural* information regarding the photolysis transition state geometry. The reaction mechanism, encoded in the VPD recorded as vibrational satellites by CP-FTmmW spectroscopy, could be deduced for any chemical reaction in which the products (i) are produced in the *gas-phase*, (ii) have a permanent dipole moment, and (iii) are *small-sized* and undergo *inefficient* vibrational cooling in the time period between the initiation of the reaction and the spectroscopic detection.