

DYNAMICS AND KINETICS STUDIED BY CHIRPED PULSE MICROWAVE SPECTROSCOPY IN COLD UNIFORM SUPERSONIC FLOWS

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The vast majority of gas-phase techniques typically employed for studying reaction kinetics follow only the time dependence of one of the reactants or the products and do not allow to distinguish between different isomers, conformers or vibrationally excited states presented in the reaction. However, this has changed in the recent years with the development of the chirped-pulse microwave spectroscopy in uniform supersonic flow (CPUF) technique to study gas phase reaction kinetics. This technique as implemented in Rennes employs the CRESU (a French acronym standing for reaction kinetics in uniform supersonic flow) method coupled with chirped-pulse Fourier transform microwave spectroscopy, combining the power to generate continuous cold uniform supersonic flows with the high selectivity and general applicability of rotational spectroscopy. As a result, it is possible to simultaneously study the time dependence of various species involved in the reaction and to distinguish between different conformers, isomers and vibrationally excited states. The uniform CRESU conditions permit frequent enough collisions to preserve local thermodynamic equilibrium in the flow with regard to translational and rotational degrees of freedom, but vibrational relaxation of some molecules may not be complete. This is a double-edged sword: a challenge for the analysis of product branching ratios, especially for strongly exothermic reactions; but also an opportunity to study vibrational relaxation of polyatomic molecules at low temperatures, a subject of significant theoretical and astrophysical interest. Here we present the time dependent collisional relaxation of some vibrationally excited states of both small molecules produced either by photolysis or chemical reaction in the cold uniform flow, as well as low frequency modes of larger molecules.