

ELEMENTARY STEPS IN INFRARED PHOTOCHEMISTRY

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Laser light sources offer a number of new ways for a controlled transfer of external energy into chemical reacting molecules. The high quantum flux, monochromaticity, coherence and short pulse duration of infrared lasers can be used to obtain new insights into the microscopic dynamics of chemical reactions by selective preparation and detection of vibrationally excited molecules. The lecture will describe several experimental investigations on vibrational energy consumption, transfer and disposal in simple gas phase reactions. Selective excitation of vibrational levels of electronic ground state molecules is achieved by optical pumping via higher electronic states and by infrared laser single and multiphoton absorption. Reactants and reaction products are detected by time-resolved infrared fluorescence, resonance absorption in the infrared and vacuum ultraviolet and nozzle beam sampling mass spectrometry. The selected examples are devoted to three aspects of elementary steps in infrared photochemistry :

- (i) Competition between chemical reaction and energy transfer in collisions of reactive atoms and vibrationally excited diatomic molecules.

In the reactions $H, D + HCl(v)$ an effective vibrational deactivation by non reactive processes as well as an increase of the rates of the exchange and abstraction reactions is observed. Fast vibrational relaxation by nonadiabatic processes and enhanced chemical reaction rates are found in the $O(^3P) + HCl(v)$ reaction. Isotopically selective reactions with a large increase of the chemical reaction rate are found in the $Cl + HCl(v=1)$

and Br + HCl($v=2$) system,

- (ii) Influence of vibrational excitation of the reactants on the product energy disposal.

The measured CO(v') vibrational energy distribution in the elementary step $O(^3P) + CN(v) \longrightarrow CO(v') + N(^4S, ^2D)$ shows, that the reaction proceeds simultaneously on two pathways.

On one path the reaction energy is converted via an intermediate complex mainly into the energy of the metastable N(2D) atom and lower states of CO(v'). On a second path a large fraction of CN(v) vibrational excitation can be converted into population of higher vibrational states in CO(v'). Experimental results are discussed in comparison with classical trajectory calculations.

- (iii) Energy flow in polyatomic molecules

Selective excitation of polyatomic molecules by infrared multi-photon absorption was observed by time resolved infrared fluorescence at low pressure. As examples the vibrational excitation of CH₃F, the isomerisation of CH₃NC and the unimolecular dissociation of N₂F₄ will be discussed.