

VIBRATIONAL SPECTROSCOPY AND CHEMICAL DYNAMICS IN REACTANT COMPLEXES OF HYDROXYL RADICALS WITH HYDROGEN AND METHANE^a

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The bimolecular reactions of hydroxyl radicals with hydrogen and methane play a fundamental role in the combustion of hydrocarbon fuels. This laboratory is examining the OH + H₂ and OH + CH₄ hydrogen abstraction reactions from a new perspective by trapping the reactants within a shallow attractive well in the entrance channel to reaction. The resultant H₂-OH and CH₄-OH reactant complexes are then vibrationally activated through infrared or stimulated Raman excitation. A variety of double resonance schemes have been implemented to record the spectra, lifetime, and product state distributions of the vibrationally activated complexes. Vibrational spectroscopy provides an effective means to examine the structural parameters of these complexes in their ground electronic state. Intermolecular bending excitation is found to control the relative orientation of the reactants within the complex, producing some that resemble the transition state structure. The OH, H₂, or CH₄ vibrational excitation also supplies sufficient energy to surmount the activation barrier and thereby may induce chemical reaction. Alternatively, the vibrational excitation can cause the weak intermolecular bond to break through vibrational predissociation. Time- and frequency-domain measurements reveal how long the initial excitation stays localized in the OH, H₂, or CH₄ mode and how excess energy is partitioned among the products. The experimental results will also be compared with theoretical calculations of the observables to yield new insights on the potential energy surfaces for the OH + H₂ and OH + CH₄ systems.

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