

ULTRAFAST ELECTRON DIFFRACTION:
DIRECT DETERMINATION OF
STRUCTURAL DYNAMICS OF
MOLECULAR EXCITED STATES

Thesis by

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Abstract

Ultrafast electron diffraction (UED) has been applied to determine the structures of isolated molecules and the dynamics of their excited states. Preceding the experimental accounts is a detailed discussion of the theoretical methodology behind UED in the Caltech labs. The procedure is explained by which electron scattering signal is measured and processed to allow the direct determination of structural dynamics (the signature feature of this experiment). The apparatus itself is also broken down into its component parts and discussed.

UED has the capability of studying both ground and excited state systems, which will be demonstrated by example. A number of molecules were studied in their ground states (chlorobenzene, bromobenzene, iodobenzene, 2-fluoropyridine, acetylacetone, benzaldehyde, acetophenone, and methylbenzoate). The structures were determined and compared with structures derived by theoretical calculations and with the results of previous gas electron diffraction inquiries. The molecular structures of 2-fluoropyridine, acetophenone, and methylbenzoate had not been previously experimentally determined. The structure of ground-state acetylacetone is discussed in detail as it represents an old problem involving the influence of intramolecular hydrogen bonding.

Acetylacetone, benzaldehyde, and acetophenone were also studied after excitation by a femtosecond laser pulse. Acetylacetone was observed to fragment – losing the hydroxyl radical. Calculations were performed to further explore the dynamics and mechanism. For excited benzaldehyde and acetophenone, a bifurcation of pathways was structurally resolved. Both molecules have photophysical and photochemical channels from the excited state. The photophysical channels result in the formation of a structure possessing a quinoid ring. The photochemical channels differed – for benzaldehyde, molecular dissociation resulting in benzene and carbon monoxide, and for acetophenone, homolytic bond cleavage resulting in methyl and benzoyl radicals. The structures of all species were determined as were the time scales involved. Calculations were used to assist in the determination of the excited state decay mechanisms.

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