CHAPTER I

INTRODUCTION

**Multidimensional Electronic Spectroscopy**

Time-resolved phase-coherent multidimensional electronic spectroscopy is a powerful tool for understanding chemical processes. Using phase-stabilized sequences of femtosecond laser pulses resonant with molecular electronic transitions, this form of nonlinear optical spectroscopy probes the ultrafast mechanisms underlying chemical dynamics.\(^1\),\(^2\) In a manner strongly analogous with multidimensional nuclear magnetic resonance (NMR) techniques, multidimensional electronic spectroscopy prepares electronic populations and coherences and monitors their subsequent time development.\(^3\)\(^-\)\(^6\) Yet, unlike the quasi-static structural information obtained from NMR, multidimensional electronic spectroscopy provides a snapshot of the molecule as it undergoes rapid configurational changes, i.e. chemical dynamics.\(^7\)

As an example, two-dimensional Fourier-transform electronic spectroscopy generates a third-order nonlinear polarization using a sequence of three noncollinear pulses.\(^8\) A fourth pulse overlapped with the subsequently emitted electric field leads to heterodyne detection of the nonlinear polarization, whence, by stabilizing the phase between the incident pulses, the real and imaginary components of the molecular response can be measured.\(^9\),\(^10\) A collection of these measurements, performed as a
function of the interpulse delays, are Fourier transformed to obtain a frequency-domain representation of the nonlinear optical response.\textsuperscript{8,11,12} Several recent experiments have implemented phase-coherent electronic spectroscopies to provide detailed pictures of the spatial and energetic dynamics found in complex molecular systems.\textsuperscript{13-15}

There are, however, many opportunities available in nonlinear optical spectroscopy without a previously defined analogy in multidimensional NMR; the femtosecond duration of the incident pulses allow the electronic populations and coherences of an excited system to be time resolved. But for a molecular system, electronic excitation by a broad bandwidth pulse also prepares time-dependent nuclear states. In these terms, the molecule’s response reflects the quantum-mechanical interference among the different, dynamic nuclear wave packets prepared by the pulse sequence and propagated under the relevant nuclear Hamiltonian(s). Moreover, from a chemical viewpoint, the nuclear dynamics undertaken by electronically-excited molecules is pertinent to a microscopic understanding of photochemical reactions; an interpretation of multidimensional electronic spectroscopy in terms of wave packet interference would be valuable for describing fundamental reaction dynamics.

In this dissertation, we develop the theory of nonlinear wave packet interferometry (WPI), an applications of multidimensional electronic spectroscopy using a wave-packet description to interpret a molecule’s nonlinear optical response. Employing a sequence of two phase-locked pulse pairs, we show how it is possible to isolate interference effects arising in an excited-electronic state population through the use of optical phase-cycling measurements. We also demonstrate that by using a wave-
packet interpretation, the isolated interference provides a means to reconstruct a time-dependent nuclear wave packet that has propagated under an ill-characterized nuclear Hamiltonian. State reconstruction has served as an organizing principle in the field of quantum optics,\textsuperscript{16} and, we believe, could also be a technique of considerable value to the understanding of photochemical reaction dynamics. For instance, our formulation of molecular state reconstruction could serve as a diagnostic complement to closed-loop, feedback-controlled pulse-shaping techniques.\textsuperscript{17-20} The latter methods determine the spectral amplitude and phase needed by an ultrashort pulse to initiate a targeted molecular response through the use of learning algorithms.\textsuperscript{21} Those experiments are often successfully employed under conditions where the Hamiltonian driving the system dynamics is ill-characterized,\textsuperscript{22,23} and a capability to perform state reconstruction in the absence of Hamiltonian information could provide insight into the quantum dynamics mediating preparation of the targeted molecular state.

**Wave Packet Interferometry**

Wave packet interferometry has been used by several groups to characterize atomic and molecular wave packets.\textsuperscript{24-34} In the original linear WPI experiments, a single pair of phase-locked and temporally-separated pulses excited a superposition of nuclear wave packets in the $B$ electronic level of gas-phase I$_2$.\textsuperscript{24,25} In an optical analogy of Young’s double-slit experiment,\textsuperscript{26} Scherer et al. showed that by measuring the contribution to the electronic population which is linear in the two applied fields, the complex-valued overlap of two nuclear wave packets could be completely resolved.\textsuperscript{24} The
first of these one-pulse wave packets, here termed the target state, is prepared by the first pulse and propagates in the excited-electronic level for the inter-pulse delay, while the second wave packet, termed the reference state, follows from the action of the second pulse. The bilinear interference collected in a linear WPI experiment as a function of the interpulse delay directly reveals the time-dependent kernel familiar from Heller’s time-dependent formulation of linear absorption, which in the short-pulse limit is equivalent to the resonant portion of the linear susceptibility. Girard and coworkers have also used the ideas of linear WPI to gain temporal coherent control over the population of both atomic and diatomic electronic levels. Ohmori et al. have employed similar ideas for the population control of a van der Waals dimer complex, and Guhr et al. have used linear WPI to monitor and control vibrational decoherence in diatomic halides trapped in rare-gas matrices. In another condensed phase application, Milota et al. have investigated homogenous dephasing processes in conjugated polymers by measuring fluorescence interference. Martínez-Galicia and Romero-Rochín have explored linear WPI from the viewpoint of the incident fields, which in a quantum-mechanical analysis, become entangled with the excited molecular system.

Although the information obtained from a linear WPI experiment alone does not completely specify the prepared nuclear wave packets, Leichtle et al. have shown how measurements of the bilinear interference can characterize a shaped vibrational wave packet using quantum state holography (QSH). In QSH, the target state is prepared by the first (possibly shaped) pulse and propagation under the excited-state Hamiltonian, while the reference state is created by the second, temporally-delayed pulse. Using
knowledge of the prepared reference states and measurements of the wave packet interference as a function of interpulse delay, QSH recast the interference data as a set of linear equations that are numerically inverted to yield the target state. Bucksbaum and coworkers have experimentally implemented a version of QSH to successfully reconstruct electronic Rydberg wave packets in cesium atoms and to guide the shaping of an optically-prepared quantum state using a closed-loop, feedback-controlled pulse-shaping technique.\textsuperscript{37} Our approach to state reconstruction outlined in subsequent chapters has much in common with QSH.

In nonlinear WPI,\textsuperscript{38-45} one detects the interference contributions to an electronic-state population excited by two pairs of phase-locked pulses. The contributions to the population linear in all four applied fields, i.e. quadrilinear contributions, arise from the quantum-mechanical interference between one-pulse and three-pulse wave packets. In previous studies of one-color nonlinear WPI,\textsuperscript{39-41} where all four pulses drive the same electronic transition, the four overlaps comprising the quadrilinear interference effect are grouped according to their phase signature: two overlaps depend on the sum of the phase-locking angles, while the remaining two depend on the difference between the phase-locking angles. Shifting the phase-locking angles allows the sign of each sum to be changed independently and, by combining population measurements taken with different values of the locking angles, the two sums can be isolated. Certain experimental conditions often minimize the mixing of individual overlaps with the same phase-signature though, in general, a single quadrilinear overlap is not completely isolable in a one-color nonlinear WPI experiment.\textsuperscript{39-41} Note also that a reconstruction scheme based on
the data obtained in a one-color experiment would require detailed information about the excited-state nuclear Hamiltonian under which both the target and reference states propagate.

The situation is different in two-color nonlinear WPI, where the first pulse-pair drives transitions between the initial electronic level and an intermediate electronic level, while the second pulse-pair drives transitions between the initial electronic level and a final electronic level. The excited-state population then contains only two quadrilinear overlaps, each with a different phase signature. Each isolable term takes the form of an overlap between a one-pulse target-state, which propagates under the presumably ill-characterized final-state Hamiltonian, and a three-pulse reference state, which propagates only in the initial and intermediate electronic levels. When the initial and intermediate potential energy surfaces are well-characterized, the reference states are known and the experimentally measured interference signal makes reconstruction of the target state possible.

Previous State Reconstruction Schemes

Several methods for reconstructing quantum states have been proposed previously. The initial experimental demonstration of quantum state reconstruction was performed by Smithey et al., who used balanced optical-homodyne tomography to reconstruct non-classical states of the electromagnetic field. Their approach was based on the theoretical work of Vogel and Risken, who showed that by measuring marginal probability distributions of the electromagnetic field for different values of the rotated
quadrature phase one can invert the data to yield a quasi-probability density function (the Wigner function) that is formally equivalent to the system’s density matrix. A similar tomographic approach using time-resolved emission spectra was put forth by Dunn et al. for reconstructing optically-prepared vibrational wave packets in diatomic molecules, provided the underlying motion was harmonic.\textsuperscript{49} Leonhardt and Raymer developed a reconstruction technique applicable to vibrational wave packets propagating in one-dimensional, anharmonic potentials, which uses measurements of the time-dependence of the position probability density and knowledge of the system’s energy eigenfunctions.\textsuperscript{50}

In another approach to the reconstruction of vibrational wave packets, Zucchetti et al. showed how the molecular polarization induced by one pulse can be characterized by mixing a second, delayed reference pulse (that does not pass through the sample) with the field radiated by the excited molecule.\textsuperscript{51} By detecting the time- and frequency-resolved interference between the reference field and the radiated field, the amplitude and phase of the expansion coefficients oscillating at known transition frequencies can be determined by numerical inversion of the measured data. This form of optically-heterodyned measurement is similar to spectral interferometry,\textsuperscript{52} which characterizes the phase and amplitude information of an unknown electric field with respect to a known reference field by mixing the two fields and spectrally-resolving the interference.

**Outline of the Dissertation**

In Chapter II, we review linear WPI, which uses a single pair of phase-locked pulses to probe excited molecular wave packets. We discuss how the one-dimensional
interferogram obtained in a linear WPI experiment represents wave-packet dynamics and we analyze the use of the linear WPI signal in an application of molecular state reconstruction.

In Chapter III, we develop the theory of nonlinear WPI for the case of one-color experiments. We equate the interference effects observed in an excited-electronic-state population to overlapping wave packets and develop an application of optical phase-cycling for isolating the interference contributions to the population. We discuss which experimental conditions enable molecular state reconstruction to be performed from a one-color interferogram. We simulate molecular state reconstruction for model harmonic and photodissociative systems by calculating the interferogram and remark on the possible uses of a one-color reconstruction technique.

In Chapter IV, we formulate the theory of two-color nonlinear WPI and determine analytic forms for the isolable interference contributions. We demonstrate how such information provides a means to perform molecular state reconstruction and discuss the advantages of two-color nonlinear WPI for applications of molecular state reconstruction, as contrasted with a one-color approach. We simulate the two-color interferogram for model harmonic and dissociative systems, as well as a realistic investigation of the lithium dimer, to investigate the effects of signal noise on reconstruction accuracy, the reconstruction of mixed-states, and the reconstruction of rovibrational wave packets.

In Chapter V, we present our results detailing an application of two-color nonlinear WPI to investigations of coherent energy-transfer processes. For a pair of $J$-coupled chromophores, we find that by controlling the phase-locking angles and the
polarization vectors of the pulses a single quadrilinear interference can be isolated. By selectively addressing the chromophores, changes in the molecular amplitude due to energy transfer are monitored. We discuss interpretations of the time-domain interferogram which describe the form of the energy-transferred target amplitude in the case of equal-site and down-hill energy transfer settings.

In Chapter VI, we include a summary of the dissertation work and speculate on what the future holds for nonlinear WPI.
Notes


