Optical Field Control of Ultrafast Dynamics in Complex Systems: Frontiers and Perspectives

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Abstract: Ultrafast optical field control has progressed from merely observing photochemical dynamics to actively steering molecular transformations. However, a persistent gap between theory and experiment continues to impede predictive control in complex systems. Femtosecond and attosecond techniques now allow real-time manipulation of electronic evolution, vibrational motions, and bond dissociation in small molecules. However, these achievements often fail to translate to condensed-phase environments due to increasing molecular complexity, environmental decoherence, and stringent instrumental constraints. This review

summarizes recent advances in which pump-probe experiments－utilizing tailored pulse parameters such as intensity, wavelength, phase, and polarization － have uncovered key control mechanisms while also revealing critical challenges in scalability and reproducibility. Theoretical progress in quantum control methods (e.g., local control theory) and mixed quantum-classical simulations has clarified fundamental principles, yet often remains disconnected from experimental implementation. We propose that machine learning (ML) serves as an essential bridge to close this gap. By constructing hybrid theory-experiment databases and training environment-aware models, ML can capture complex pulse-branching correlations and system-environment couplings. These models effectively translate theoretical insights into experimentally feasible pulse designs, thereby paving the way for designing light-driven molecular processes that extend beyond gas-phase paradigms to functional materials.
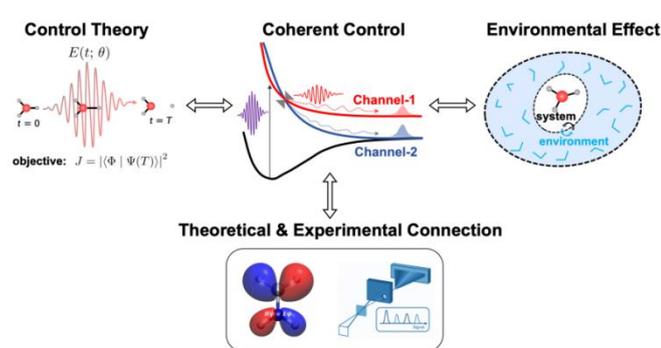
Key words: optical field control, pump-probe spectroscopy, coherent control, nonadiabatic dynamics.

1. Introduction

Ultrafast laser technologies have transformed photochemistry from passive observation to active control, meaning the deliberate shaping of laser pulses to influence reaction pathways, evolving from 1970s isotope separation to 1980s quantum pathway manipulation [1-3]. The 1990s breakthrough of femtosecond pump probe techniques enabled direct imaging of transition states, earning the 1999 Nobel Prize and establishing light-driven control as a cornerstone of modern physical chemistry [4]. Today, femtosecond and attosecond pulses steer electronic and nuclear dynamics at natural timescales, positioning ultrafast photochemistry at the forefront of atomic-scale molecular engineering [5-7].

A few systems have successfully demonstrated coherent control of phenomena such as electronic relaxation and bond dissociation in the gas phase. However, this very success also reveals a critical limitation: experimental control remains system-specific due to incomplete knowledge of high-dimensional potential energy surfaces (PESs) [8,9]. Early studies proved the concept but exposed a fundamental gap between theoretical principles and experimental generalizability, driving advances in quantum dynamics that now enable rational pulse design [10]. As the field expands to larger π-conjugated and biologically relevant systems, novel light sources offer unprecedented manipulation opportunities [11]. Yet dense electronic manifolds, environmental decoherence, and condensed-phase pulse distortions impede robust control, highlighting the persistent theory-experiment disconnect [12]. Prior reviews have effectively summarized experimental strategies and applications in photochemical control [13,14], but a systematic analysis of molecular dynamics-a critical perspective for predictive control-has remained relatively limited.

We bridge this divide by organizing the review around dynamical processes rather than control methods alone. Tracing the transition from gas-phase to condensed-phase systems, we show how theory must evolve to address environmental complexity. Crucially, we advance emerging frontiers like machine learning-assisted pulse optimization and environment-aware modeling to demonstrate how theory now guides experimental design. By synthesizing these advances, we establish a predictive framework for optical field control in complex systems — moving beyond

cataloging phenomena to actionable control pathways. The remainder of this review is organized as follows. Section 2 surveys key experimental advances in optical-field-controlled molecular dynamics. Section 3 introduces the corresponding theoretical frameworks that simulate these processes and elucidate the underlying mechanisms. Section 4 discusses emerging machine-learning strategies that connect theoretical insight with experimental constraints to enable scalable optical field control.
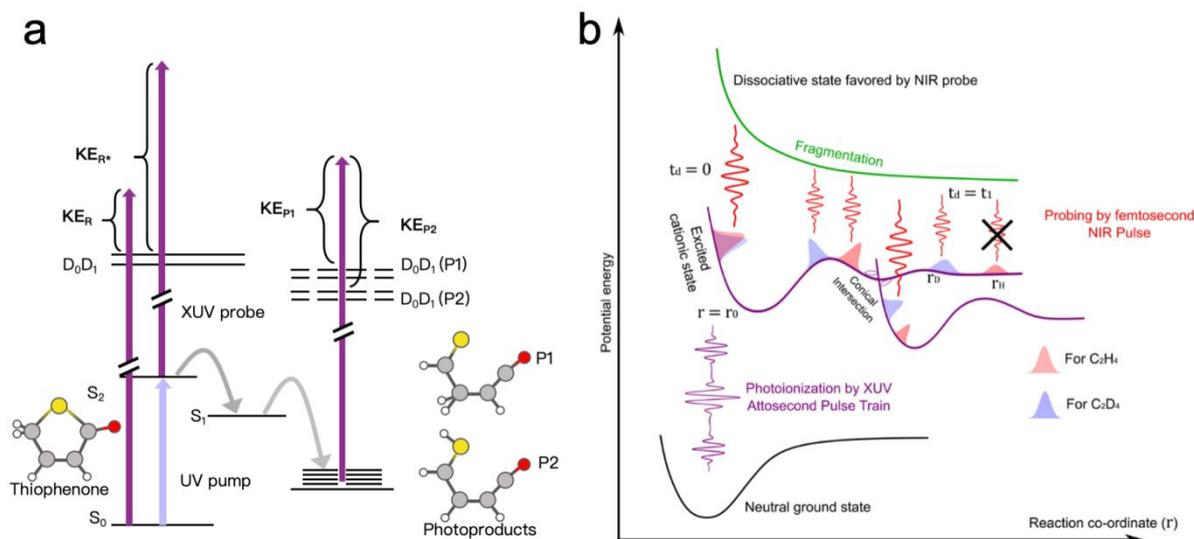
Figure 1. (a) UV pump and XUV probe tracking the ring-opening dynamics of thiophenone, showing relaxation via $S_2 \rightarrow S_1 \rightarrow S_0$ and subsequent formation of open-chain photoproducts (ref [15]). (b) Attosecond XUV pump-NIR probe experiment on ethylene isotopologues, revealing isotope-dependent relaxation dynamics. Adapted with permission from ref [16]. *Copyright © 2022, American Chemical Society.*

2. Coherent control of photochemical reactions

2.1 Pump-probe studies in small molecules

Small molecular systems, such as IBr, CH_4, C_2H_4, and CH_3I, serve as ideal models for validating laser field control strategies, owing to their well-defined electronic structures and low-dimensional PESs. These systems provide a foundational platform for elucidating fundamental photophysical and photochemical processes, including electronic relaxation, nonadiabatic transitions, and bond-selective dissociation, showing direct insights into ultrafast reaction dynamics under tailored optical fields [17]. In recent years, advances have transformed theoretical principles into experimental reality. For instance, Wei et al. observed large-amplitude vibrational wave packets and dissociative ionization in strong-field ionized CH_2I_2, revealing nonadiabatic dynamics under intense laser excitation [18]. Ridente et al. employed femtosecond X-ray free-electron lasers to track symmetry breaking and coherent relaxation in the CH_4^+ cation in real time [19]. Additionally, González-Vázquez et al. combined synchrotron radiation with double imaging photoelectron photoion coincidence spectroscopy techniques to capture the conical intersection involved in the internal conversion of CH_3I^+ [20]. Together, these studies confirm that small molecules exhibit rich ultrafast dynamics and demonstrate the critical role of advanced light sources in probing and controlling photochemical pathways.

Building on this foundation, we highlight several representative pump-probe studies that exemplify how advanced

light sources bridge molecular dynamics and control theory. As shown in **Figure 1a**, Pathak et al. used a ultraviolet/extreme ultraviolet (UV/XUV) experiment in gas-phase thiophenone, where a 265 nm pump initiated S_2 excitation and a 19.24 eV XUV free-electron laser probe tracked ultrafast ring opening via time-resolved photoelectron spectroscopy [15]. The resulting spectra reveal a C-S elongation and ring opening within ≤ 350 fs through the $S_2 \rightarrow S_1 \rightarrow S_0$ nonadiabatic pathway, followed by isomer interconversion and delayed fragmentation on vibrationally hot S_0 (10-600 ps). Critically, this trajectory — which maps directly onto a conical intersection—provides direct experimental validation of theoretical predictions for nonadiabatic reaction pathways. Beyond these femtosecond pump-probe experiments, attosecond-resolved studies further extend ultrafast spectroscopy into the electronic timescale. Representative examples include attosecond high-harmonic charge-migration spectroscopy in N_2/CO_2, chiroptical measurements of methyloxirane, and vibrationally resolved reconstruction of attosecond beating by interference of two-photon transitions (RABBIT) delays in CO_2 [21-23]. Collectively, these studies show that attosecond spectroscopy can quantify electronic, chiral, and mode-specific electron-nuclear dynamics on their natural timescales. As another example, **Figure 1b** highlights an approach of attosecond XUV pump with an NIR probe by Vacher et al., where an at tosecond XUV pulse pumped ethylene cations to multiple excited states, while a near-infrared (NIR) probe resolved few-femtosecond nuclear dynamics and electron-nuclear coupling [16]. By comparing protiated and deuterated isotopologues, the study established the first experimental benchmark for electronic-timescale isotope effects — a key test for quantum dynamics