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LETTERS

Multiphoton Intrapulse Interference. 1. Control of Multiphoton Processes in Condensed Phases

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We explore and demonstrate the use of phase-modulated ultrafast laser pulses for controlling nonlinear optical processes in large molecules, proteins, and solid materials. Our experiments illustrate that in condensed phases, when spectra are broad, the spectrum of the *n*th-order electric field, determined by multiphoton intrapulse interference, plays a major role in controlling multiphoton excitation. These findings determine key parameters (amplitude, period, and symmetry of the phase function) for coherent femtosecond laser control in condensed phases.

I. Introduction

Nonlinear optical interactions of laser fields with matter are of fundamental importance in the understanding and design of spectroscopic tools, contrast methods for microscopy, photochemistry, and optoelectronics. It is presently unclear to what extent efficient laser control is possible when dissipation must be accounted for as in the liquid phase.[1] In this report, we explore the conditions under which control over nonlinear processes can be achieved using well-defined phase functions imprinted on ultrafast laser pulses.[2]

Progress in the field of laser control has accelerated rapidly during the past decade. Quadratic phase modulation (linear chirp in the time domain), for example, has been found to optimize population transfer and the yield of chemical reactions.[3−7] A simple sine or step phase function has been used to minimize two-photon absorption of rubidium,[8,9] cesium,[10,11] and sodium atoms.[12] Pulse shaping technology, allowing control of the phase and amplitude of a discrete number of frequencies across the bandwidth of ultrafast laser pulses, has revolutionized the types of experiments that can be carried out.[13] Pulse shapers together with computer learning algorithms have been used to control the outcome of chemical reactions in the gas phase[14,15] and multiphoton excitation in condensed phases.[16−21] Learning algorithms, however, often yield phase functions that are difficult to interpret; therefore, the control mechanism cannot be identified. The approach presented here follows a physical description of nonlinear optical processes that combines the nonlinear excitation spectrum of the system with the spectra of the *n*th-order electric field of the laser to design and evaluate the phase function required with a minimum number of parameters. Our results demonstrate large changes (from a factor of 2 to 3 orders of magnitude) in multiphoton-induced processes. The control process is robust and can be predicted with the theory included here.

II. Theory

The phase across the spectrum of an ultrafast pulse can affect the multiphoton process in a number of ways. Phase can increase the pulse length and hence reduce the peak intensity of the pulse, thereby preventing saturation, a common result under high-intensity excitation. Phase can also be used to synchronize changes in the electric field with intramolecular wave packet dynamics. This idea has been explored theoretically and invoked to explain some gas and condensed phase experiments. Finally,

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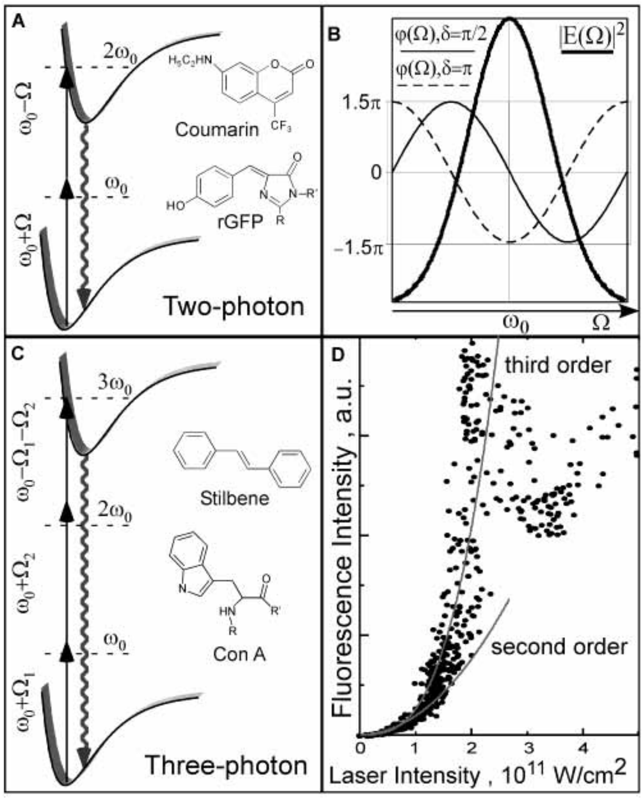

Figure 1. Schematic representation of two-photon (A) and three-photon (C) induced fluorescence and structures of some of the chromophores investigated. Ultrafast pulses have a broad bandwidth (B), with spectral components detuned from the central wavelength ω_0 by an amount Ω. Pulse shaping is achieved with a phase mask defined by eq 4 across the pulse spectrum. (D) Power dependence of laser-induced fluorescence obtained for coumarin 535. Notice that the initial quadratic increase in fluorescence with laser intensity gets steeper before it reaches a maximum and begins to decrease.

phase can be used to cause interference in the way multiple frequencies combine to achieve multiphoton excitation. This process also known as multiphoton intrapulse interference (MII) has been demonstrated under sharp resonance conditions such as transitions in isolated atoms.[8,9] Here we explore phase modulation strategies that can be used to control multiphoton processes in large molecules. We focus in particular on the MII process.

The underlying concept of intrapulse interference is shown in Figure 1. Multiphoton transitions are optimized when the central bandwidth of the laser pulse, ω_0, is some fraction (half for two-photon, a third for three-photon, etc.) of the total energy of the transition (see Figure 1). For ultrafast pulses, when the bandwidth is large, different frequency components ($\omega_0 + \Omega$) of the pulse can interfere to focus the spectral energy on a particular frequency.[9] This concept assumes a sharp absorption resonance; therefore, it has been considered only applicable to control transitions in isolated atoms.[22] It has been assumed that intrapulse interference does not work on systems with a broad resonance because the strict resonance condition is lost.[11] Here we show that multiphoton intrapulse interference can play an important role in controlling multiphoton processes in the absence of sharp resonances.

In Figure 1B the spectrum of the ultrafast laser spectral amplitude, $|E(\Omega)|$, is plotted as a function of detuning from the central frequency. A phase mask, $\varphi(\Omega)$, can be imprinted on the pulse such that the phase of each frequency component, Ω, acquires a specific value. The effect of pulse shaping on the probability amplitude for two-photon absorption (2PA) can be calculated as follows:[9,11] first we evaluate the second-order electric field spectrum (frequency response) as a function of detuning $\Delta = \omega - n\omega_0$ with $n = 2$,

$$A^{(2)}(\Delta) \propto \int_{-\infty}^{\infty} |E(\Omega)|\,|E(\Delta-\Omega)| \exp[i\{\phi(\Omega) + \phi(\Delta - \Omega)\}]\, d\Omega \tag{1}$$

For n-photon absorption (nPA) a similar formula can be derived,

$$A^{(n)}(\Delta) \propto \int_{-\infty}^{\infty}\ldots\int_{-\infty}^{\infty} d\Omega_1\ldots d\Omega_{n-1}\, |E(\Omega_1)|\ \ldots\ |E(\Omega_{n-1})| \times |E(\Delta-\Omega_1\ldots-\Omega_{n-1})| \exp[i\{\varphi(\Omega_1)\ \ldots + \varphi(\Omega_{n-1}) + \varphi(\Delta-\Omega_1\ldots-\Omega_{n-1})\}] \tag{2}$$

where amplitudes and phases are introduced for the intermediate detuning values Ω_1 through Ω_{n-1} (see Figure 1C). The signal resulting from an n-photon absorption process is then calculated using the equation

$$S^{(n)} \propto \int_{-\infty}^{\infty} g^{(n)}(\Delta)|A^{(n)}(\Delta)|^2\, d\Delta \tag{3}$$

which convolves the nth-order spectral amplitude of the laser pulse with the nth-order absorption spectrum of the system $g(\Delta)$. Here we assume that excitation probability does not depend on the phase of $A^{(n)}(\Delta)$.

A rational approach to introducing intrapulse interference in multiphoton transitions of large molecules requires phase functions that are comparable to the homogeneously broadened absorption spectrum and the spectral width of the pulse. Conversely, in the time domain, the shaped pulse should be comparable to the coherence relaxation dynamics of the material. Here we used the following formula for defining the phase function,

$$\varphi(\Omega) = \alpha \cos(\gamma\Omega - \delta) \tag{4}$$

where α is the phase amplitude (retardation), γ is the modulation in the frequency domain $2\pi N/(\Omega_{\max} - \Omega_{\min})$ with period N, and δ is the position of the phase mask with respect to the center of the pulse spectrum.

In Figure 1D, we show the power dependence of multiphoton laser-induced fluorescence (LIF) observed from a solution of Coumarin 535 laser dye obtained using transform limited (TL) pulses. For low intensities there is a quadratic dependence expected for two-photon excitation. At higher intensities, a cubic dependence can be noted, caused by three-photon excitation. At saturation, further increases in intensity cause a decrease in observed fluorescence. It is clear that at or near saturation phase modulation can be used to lengthen the pulse so that the fluorescent state is no longer saturated. The experiments presented in this article were obtained well below saturation. Below saturation and in the absence of intermediate resonances, multiphoton processes are maximized by TL pulses. Experimental results that contradict this statement may indicate the transition was saturated or that the pulses had some residual cubic chirp. The introduction of phase as a means of increasing the pulse length to prevent saturation of a multiphoton process is a rather trivial application of coherent control and is not explored here.

III. Experimental Section

Experiments were carried out using an amplified titanium sapphire laser producing 50 fs pulses near TL. The pulses were

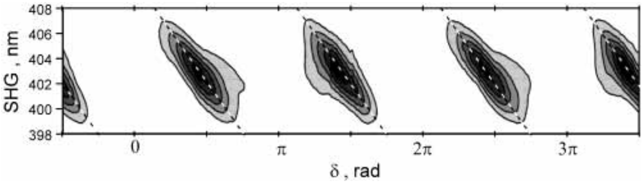

Figure 2. Experimental frequency dispersed second harmonic emission as a function of phase mask parameter δ. Darker shading indicates higher intensity. Notice that changes in δ lead to tuning of the frequency in the second-order electric field amplitude.

shaped using a spatial light modulator (SLM) at the Fourier plane of a zero-dispersion two grating arrangement.[13] The two independent modulator plates were calibrated so that only phase delays were introduced without changes to the output spectrum, intensity, and polarization. The shaped pulses centered at 800 nm were characterized by second harmonic generation frequency resolved optical gating.[23] Laser pulses were near TL when all phases were set to zero. Measurements were made with peak intensities ranging from 10^9 to 10^{11} W/cm^2 for TL pulses. Experiments were carried out by setting the phase function according to eq 4 with $\alpha = 1.5\pi$ (approximately 2 fs), $N = 1$, and scanned as a function of δ, as shown in Figure 1B, in the 770−830 nm spectral range. Emission from one-photon- or multiphoton-induced processes from all samples was measured as a function of δ.

The following samples were used: 10^{-4} M solution of IR144 (Exciton) in methanol; 10^{-4} M solution of coumarin 460 (C460) (Exciton) in methanol; and a 10^{-5} M solution of coumarin 535 (C535) (Exciton) in methanol; 10^{-2} M solution of coumarin 500 (C500) (Exciton) in methanol; 1 mg/mL solution of recombinant green fluorescent protein (rGFP) in 10mM Tris−HCl (Clontech Laboratories); 10^{-2} M solution of *trans*-stilbene (Eastman) in methanol; 50 mg/mL solution of concanavalin A (Con A) (Bohringer Mannheim) in 50 mM HEPES; 10^{-3} M fluoranthene (99%, Aldrich) solution in acetone. Sample solutions were irradiated in 1 or 10 mm path quartz cells and were practically transparent to the laser.

IV. Results

The MII process has been demonstrated in the literature for systems with sharp resonances, such as atomic transitions, and for second harmonic generation. Because of our interest in control of large molecules in condensed phases, we explore the MII processes in systems with broad absorption spectra. The first step is to visualize the effect of phase on the *n*th-order electric field amplitude $A^{(n)}(\Delta)$. This can be done experimentally by measuring the second harmonic generation (SHG) spectra. If the SHG crystal were infinitely thin, we would obtain directly $|A^{(2)}(\Delta)|^2$; otherwise the phase matching conditions would need to be taken into account[26,27] to obtain $g^{(2)}(\Delta)|A^{(2)}(\Delta)|^2$. In Figure 2 we illustrate the MII process as observed following irradiation of a thin 0.3 mm β-barium borate crystal cut for type I SHG. The experimental data (contours) show how the frequency doubled light scans from 407 to 399 nm as δ is scanned (from longer to shorter wavelengths) across the spectrum of the pulse. Notice that in eq 1, the phase condition (in the exponent) is maximized for all situations when $\varphi(\Omega) = -\varphi(-\Omega)$. In the absence of a resonance, the maximum occurs at the frequency where the exponent vanishes. Therefore, the frequency of maximum SHG tracks δ. Figure 2 (see dashed lines obtained from theory) illustrates how phase modulation can be used to "focus" the energy of a multiphoton process to a particular frequency; this effect can be used to control multiphoton transitions in large molecules. MII not only causes energy focusing but can also be used to cause energy spreading, or the formation of multiple peaks. When $\varphi(\Omega) = \varphi(-\Omega)$, for example for $\delta = 0$, the phase contribution in eq 1 is minimized, the spectrum is maximally spread, and the intensity is minimized. We have found that scans such as the one shown in Figure 2 are extremely sensitive to the laser pulse characteristics. Quadratic or cubic phase distortions across the pulse spectrum result in changes in the feature spacing and angle, respectively.

The data presented in Figure 3 show the two-photon LIF intensity as a function of phase mask position δ for two different laser dyes. Solutions of C460 and C535 in methanol have absorption bands centered at 370 and 435 nm, respectively; see Figure 3a. These dyes were chosen because their two-photon absorption spectrum is very similar to their single photon absorption spectrum.[26] The data in Figure 3 were obtained with unfocused laser light $\sim 10^9$ W/cm^2.

The data in Figure 3b shows two traces, one obtained for C460 (solid dots) and the other for C535 (open dots) as a function of δ. Simulations, shown in Figure 3c were obtained with eqs 1 and 3 using the experimental absorption spectra for $g^{(2)}(\Delta)$, and the spectrum of the laser pulse (no adjustable parameters). The data and simulations were normalized such that the signal intensity observed with transform limited pulses equals unity and the background observed with the laser blocked (a very small of number of dark counts from the cooled CCD detector) is zero. First we notice that the signal achieves a maximum for $\delta = \pi/2$ and $3\pi/2$. Minima are observed for $\delta = 0$, π, and 2π. This observation is consistent with the intensity of the SHG output observed in Figure 2. Here we concentrate on the shift that is observed between the two different dyes. Because of MII effects, the two-photon energy scans from longer to shorter wavelengths and this is reflected in the shift between the two traces. The difference between the two different dyes

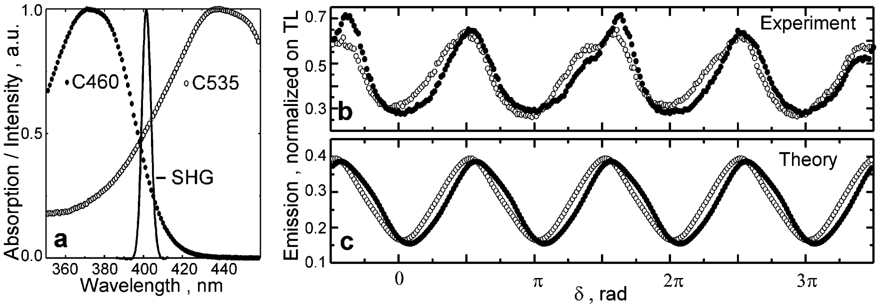

Figure 3. Two-photon laser-induced fluorescence from coumarin 460 (solid dots) and coumarin 535 (open dots) as a function of phase mask position δ. The absorption spectra of the two dyes are shown in panel (a) together with the spectrum of the second harmonic of the TL laser pulses. The experimental data (b) obtained as a function of phase parameter δ show a shift in phase for both molecules caused by differences in their excitation spectrum and the MII process. Notice that the experimental data are in very good agreement with the theory (c).

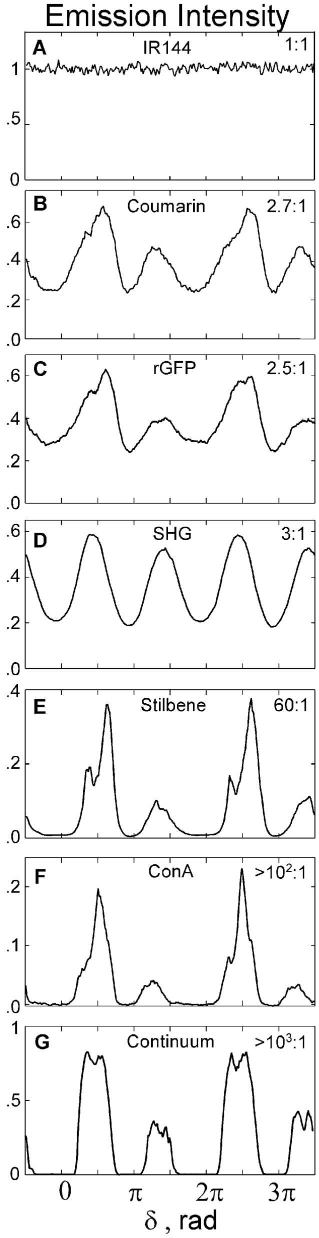

Figure 4. Experimental measurements of one-photon and multiphoton emission obtained as a function of phase parameter δ. The signal measured with transform-limited pulses is normalized to unity. (A) One-photon laser-induced fluorescence from IR144. The next three panels show two-photon emission corresponding to (B) coumarin 500, (C) recombinant green fluorescent protein, and (D) second harmonic generation. The three-photon-induced fluorescence from *trans*-stilbene and Con A is shown in (E) and (F), respectively. The data in (G) correspond to continuum generation. The contrast ratio (max:min) is given in the upper right corner of each of the experimental plots.

was explored for different values of α and N, for different concentrations, and for different laser intensities. In all cases, the sign of the difference was consistent. The shift observed in Figure 3 indicates that MII can be used to selectively control the multiphoton excitation of large organic molecules in solution, contrary to earlier expectations.

Experimental results for various samples are shown in Figure 4. Figure 4A shows the one-photon LIF of IR144 observed at 842 nm as a function of phase mask position. This measurement was made with ~10^{10} W/cm^2 TL peak intensity. No dependence on phase shaping was observed at this intensity. Figure 4B shows results for the two-photon LIF from C500 collected at 500 nm. The data in Figure 4C show the dependence of two-photon LIF in rGFP detected at 505 nm. The data in Figure 4D correspond to the intensity of the SHG signal from a 0.3 mm β-barium borate crystal. The maximum and minimum signals for SHG coincide with those observed for two-photon LIF but are not identical. It is striking that the data obtained for C500 and for rGFP are so similar. In fact, the similarity is such that one may be able to conclude that for such large molecules, coherent control based on 50 fs pulses cannot address directly the intramolecular dynamics. This point will be discussed further in the conclusions.

In Figure 4E we show the dependence of three-photon LIF from *trans*-stilbene collected at 350 nm. In this case, the maximum contrast (max:min) is measured to be 60:1. The data in Figure 3F correspond to the three-photon LIF from tryptophan residues in Con A collected at 350 nm. There is a minimal difference between the stilbene and Con A signals, indicating that intramolecular dynamics in these very different molecules play a minor role for three-photon excitation, as found above for two-photon excitation. Notice that the higher the order of the optical nonlinearity the greater the contrast observed; therefore, discrimination among different order processes is possible. The data in Figure 4G correspond to the continuum generation response (a nonlinear self-frequency modulation process yielding white light pulses[27]) from a 3 mm slab of quartz detected at 600 nm.

Suppression of nonlinear processes induced by ultrafast pulses is being pursued with great interest in the communications community, where nonlinearities lead to loss of fidelity and information.[28] Using two detectors, we set up a number of experiments similar to those in Figure 4 to explore to what extent we could suppress higher nonlinear optical processes using MII under high photon flux conditions. We found that continuum generation in the dye solution was very sensitive to the phase and could be suppressed entirely over a broad range of δ even for 1 μJ pulses (~10^{11} W/cm^2 when TL) focused on the sample. Under those conditions, we were still able to collect two-photon signals.

V. Discussion

This work explores coherent control of large molecules including proteins in solution. In contrast to recent publications in the field, where a learning algorithm is used to optimize a particular observable, we have carried out a number of well-defined measurements to elucidate the key requirements for coherent control in condensed phases. Most importantly, we have shown that multiphoton intrapulse interference can play an important role in coherent control of large molecules in solution. For our experiments, we used a phase function with only three parameters, allowing us to quickly find what value they should take on the basis of the molecular system. We have found that the best results were observed with a phase modulation amplitude of 1.5 π. Ideally, there should be one period in the phase function across the spectrum of the laser, such that half a period should roughly equal its full-width at half-maximum. The spectrum of the laser pulse should overlap the frequencies corresponding to the nth-order processes being controlled. This implies that coherent control in the condensed phase will be enhanced for molecules with narrower absorption bands or using very short pulses (with very broad spectral bandwidth).

The second most important observation of our work is that intramolecular dynamics, such as the coherent vibrational wave packet motion following excitation, seem to play a minor role in these experiments. Our results seem to negate the idea that the shaped pulse is synchronized to intramolecular dynamic processes. We reach this conclusion by comparing results between dye molecules and proteins following two-photon (Figure 4B,C) and three-photon (Figure 4E,F) excitation. Both types of systems have completely different molecular structures yet show very similar dependence on phase. The similarity of their responses to phase modulation indicates that in the condensed phase, when spectra are broad, the spectrum of the *n*th-order electric field (determined by multiphoton intrapulse interference) plays a major role.

The concept that a complex phase modulation is required to control large molecules in the condensed phase is not in agreement with our findings. When the phase was modulated with a function that was narrower in the frequency domain than the full width at half-maximum of our laser pulse spectrum, the nonlinear optical signal decreased substantially. Under high-intensity excitation, phase modulation can provide a simple mechanism to lengthen pulse duration and hence prevent saturation. If phase modulation is used to provide attenuation, then a number of different phase functions could be used to produce the desired attenuation. This would imply that the search for an “optimum” laser pulse would not yield a unique result. The saturation regime has not been considered here. We can conclude from our study that “optimum” coherent control of large molecules in solution may not involve a unique pulse with a complex phase modulation function. We find the main features required of phase functions to optimize a particular process on the basis of simple guidelines determined from the absorption spectrum of the molecule and the *n*th-order spectrum of the pulse.

If we expand the phase function in a Taylor series centered on the carrier frequency of the laser, the first term (that is not constant) is linear for a sine function and quadratic for a cosine function; see Figure 1B. A linear phase function would be equivalent to no phase modulation (would only cause a time delay) and the quadratic term would provide a linear chirp in the time domain. On the basis of the parameters used in our experiments, when the phase mask looks like a sine function, there is a significant focusing of the second-order electric field spectrum caused by the asymmetry and phase interference. This focusing does not take place with a purely linear phase function, regardless of slope. When the sine function is scanned within the pulse spectrum the focused intensity scans in frequency. The second-order electric field spectrum resulting from quadratic chirp is also different from that resulting from a cosine function. We have explored the resulting electric field spectrum for a number of phase functions including the combinations of a cosine functions and quadratic chirp. Results from that study in relation to control of two- and three-photon excitation of large molecules in solution are presented elsewhere.[29] The experimental observations presented in this work cannot be explained by effects of quadratic chirp. MII has been exploited until now to control atoms and second harmonic generation, and here we show how to apply it to large molecules in condensed phase.

Although our calculations are in close agreement with the experiments, the modulation in the nonlinear optical signal, especially for third-order and higher processes is greater than expected. These observations (see Figure 4) indicate that a number of additional nonlinear processes are operating in concert. We suspect that self-focusing, self-phase modulation, and some internal dynamics are taking place as well.

The experiments presented demonstrate that selective control of one- and multiphoton processes in large molecules, including proteins, is possible by designing the field according to the nature of the physical process and the properties of the molecules. The method is robust and predictable, provides macroscopic results visible by eye, and is applicable in condensed phases. The effect shown in Figure 3 is small, but we consider it the tip of the iceberg. Multiphoton intrapulse interference is not just about focusing the energy. The goal is to determine the field that the molecules experience. Because this high-order field can be tailored to take any shape, the work presented here gives us a foundation to design a number of experiments. The control of nonlinear optical processes, as demonstrated here using multiphoton intrapulse interference can be applied in diverse fields such as photochemistry, communications, and medicine. Our experimental observations and theory promise a greater understanding of coherent control experiments, their extension to condensed phases, and applications.

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