Coherent Control of Bond Making

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We demonstrate for the first time coherent control of bond making, a milestone on the way to coherent control of photo-induced bimolecular chemical reactions. In strong-field multiphoton femtosecond photoassociation experiments, we find the yield of detected magnesium dimer molecules to be enhanced for positively chirped pulses and suppressed for negatively chirped pulses. Our ab initio model shows that control is achieved by purification via Franck-Condon filtering combined with chirp-dependent Raman transitions. Experimental closed-loop phase optimization using a learning algorithm yields an improved pulse that utilizes vibrational coherent dynamics in addition to chirp-dependent Raman transitions. Our results show that coherent control of binary photo-reactions is feasible even under thermal conditions.

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A long-standing yet unrealized dream since the early days of coherent control, about 30 years ago, is the coherent control of photo-induced bimolecular chemical reactions [1, 2]. Realizing this dream will create a new type of photochemistry with selective control of yields and branching ratios [3, 4]. Shaped femtosecond laser pulses act there as special "photo-catalysts" with a first pulse inducing and controlling the formation of a chemical bond, and a second time-delayed pulse breaking the desired bonds within the generated molecule. The second step, photodissociation into target channels with the desired branching ratios, has been demonstrated early on [5, 11], once femtosecond lasers and pulse shaping technology became available. On the other hand, and in striking contrast, no study has previously demonstrated coherent control of bond making. The photo-induced creation of a chemical bond between the colliding reactants, also termed photoassociation, using femtosecond laser pulses has proven to be much more challenging [12–16]. Particularly at high temperature, a typical situation for chemical reactions, the starting point for photoassociation is rather unfavorable to coherent control since many scattering states are incoherently populated. A necessary requirement for the coherent control of photoassociation is thus preparation of quantum states with some coherence. Key are vibrational coherences in the desired bond. As we have previously demonstrated with two-photon femtosecond photoassociation of hot magnesium atoms [16, 17], such coherences can be generated by Franck-Condon filtering of quantum correlated states, exploiting correlations between rotational and translational motion in the initial incoherent thermal ensemble. These coherences should be amenable to coherent control.

Here we demonstrate coherent control of bond-making in strong-field multiphoton femtosecond photoassociation (PA) of hot magnesium atoms. Our experimental results show the PA yield of detected Mg$_2$ molecules to be coherently controlled by linearly chirped pulses: The yield is strongly enhanced, compared to an unshaped transform-limited pulse, by positively chirping the pulses, and significantly suppressed for negatively chirped pulses. The measured PA yield is further enhanced by performing a closed-loop phase optimization of the best positively chirped pulse, using a genetic algorithm. Our ab initio model reveals the control mechanism to include purification via Franck-Condon filtering of collision energies and partial waves, chirp-dependent coherent Raman transitions, and vibrational coherent molecular dynamics. Our results prove that coherent control of binary photo-reactions is feasible even under thermal conditions.
The bond-making excitation scheme for the free-to-bound PA process, \( \text{Mg} + \text{Mg} + h\nu \rightarrow \text{Mg}_2 \), is shown in Fig. 1(a). Pairs of magnesium atoms, part of an ensemble held at a temperature of 1000 K, collide in the \( X^1\Sigma^+_g \) ground electronic state and are photoassociated via multiphoton transitions by an intense phase-shaped near-infrared femtosecond pulse. The laser pulse is of linear polarization, 840 nm central wavelength, 13 nm bandwidth, and 70 fs transform-limited (TL) duration. For the linearly chirped pulses, the spectral phase of the pulse is of the form \( \Phi(\omega) = \frac{1}{2} k(\omega - \omega_0)^2 \) with \( \omega_0 \) the central frequency and \( k \) the linear chirp parameter. The PA process involves a broadband free-to-bound non-resonant two-photon transition from the \( X^1\Sigma^+_g \) state to the excited \( (1)^1\Pi_g \) state as well as strong-field dynamics and resonant dipole transitions between the latter and higher-lying electronically excited states. The pulse shape controls the PA dynamics and the final populations of the various electronically excited states. Within this manifold, bound rovibrational levels of the \( A^1\Sigma^+_u \), \( (2)^1\Sigma^+_u \) and \( (1)^1\Pi_u \) states emit UV light at 285.5–350.0 nm, below the \( 1P \rightarrow 1S \) line of the Mg atom at 285.3 nm. The corresponding integrated UV intensity \( I_{UV} \) is proportional to the total population in these molecular states, reflecting the corresponding PA yield of Mg\(_2\) molecules. This population is our control objective.

Experimentally, magnesium vapor of about 5 Torr partial pressure in a heated cell with argon buffer gas is irradiated by a shaped laser pulse. The shaping was done using a liquid-crystal spatial light phase modulator \([18,19]\). The UV radiation emitted toward the laser-beam entrance to the cell is collected at a small angle from the laser-beam axis using a proper optical setup.

Coherent control of femtosecond photoassociation is demonstrated in Fig. 1(b) by plotting the UV signal \( I_{UV} \), normalized with respect to the signal obtained for the TL pulse (\( k = 0 \)), versus the chirp parameter \( k \). An overall high degree of chirp control and a strongly asymmetric chirp dependence are observed. In particular, a large enhancement is obtained for positively chirped pulses whereas negatively chirped pulses lead to strong suppression. The chirp enhancement \( (E) \) also exhibits an intensity dependence, which is a clear indication of the strong-field regime: As the pulse energy, or, equivalently, the peak TL intensity \( I_{TL} \), increases, the maximal enhancement \( E_{max} \) and the corresponding chirp \( k_{max} \) become larger. We find \( E_{max}=4.2 \) at \( k_{max}=0.004 \) ps\(^2\) and \( E_{max}=5.4 \) at \( k_{max}=0.006 \) ps\(^2\) for \( I_{TL} = 5.0 \times 10^{12} \) W/cm\(^2\) and \( 7.2 \times 10^{12} \) W/cm\(^2\), respectively. Since two linearly chirped pulses, one of positive chirp \(|k|\) and the other of negative chirp \(-|k|\), have identical instantaneous temporal intensity but different instantaneous temporal frequency and phase, the degree of coherent control is best reflected by the enhancement ratio \( E(k_{max})/E(-k_{max}) \). It amounts here to about 40 for \( I_{TL} = 7.2 \times 10^{12} \) W/cm\(^2\), i.e., the experimentally observed PA yield is enhanced by this factor for the positively chirped pulse with \( k = k_{max} = 0.006 \) ps\(^2\) as compared to the negatively chirped pulse. This striking evidence of phase control calls for an explanation in terms of the underlying quantum molecular dynamics.

Our first principles modeling of the multiphoton PA process utilizes the theoretical framework of Ref. [17], combining \textit{ab initio} electronic structure theory with quantum molecular dynamics for the Mg\(_2\) molecule in the presence of a strong laser field and thermal averaging based on random phase wavefunctions. Here, we extend the model of Ref. [17] and explicitly account for all electronic states shown in Fig. 1(a), in order to improve the treatment of the Stark shifts for the electronically excited states. The UV emission signal \( I_{UV} \) is calculated from the final populations of the appropriate states, \( A^1\Sigma^+_u \), \( (2)^1\Sigma^+_u \) and \( (1)^1\Pi_u \), via their Einstein coefficients. These electronic states have a significant electronic transition dipole moment to the \( X^1\Sigma^+_g \) state and rovibrational levels that are located below the \( 1P + 1S \) atomic threshold, giving rise to emission at wavelengths larger than 285.3 nm.

As Fig. 1(b) shows, our theoretical model clearly reproduces the main features of the experimental results — enhancement of the signal for positive chirp and suppression for negative chirp. The dependence on intensity, i.e., the larger values of \( E_{max} \) and \( k_{max} \) for larger intensity, is also predicted qualitatively correctly by the calculations. Quantitatively, the simulations show a slightly smaller peak enhancement, \( E_{max}=4.5 \) instead of 5.4 for the larger intensity; and the maximum is located at larger chirps compared to the experimental data. The discrepancy with respect to \( E_{max} \) can easily be resolved by a small scaling of the \( (1)^1\Pi_g \) Stark shift. For example, scaling this Stark shift by a factor of 0.95, well within the estimated error bounds of the calculated polarizabilities, increases \( E_{max} \) from 4.5 to 5.8. On the other hand, the shift in \( k_{max} \) is most likely linked to the relative slopes of the potentials of the \( (1)^1\Pi_g \) state and all highly excited states that are accessed from it. Due to the number of electronic states that are involved, it is not possible to identify a single or few parameters whose change would result in an improved model. The inaccuracy of the highly excited states of Mg\(_2\) in our model is confirmed by recent spectroscopy \([20]\) which revealed the well depth of the adiabatic \( (1)^1\Pi_g \) state to be larger by nearly 50% than the original \textit{ab initio} result \([15]\). This inaccuracy is not surprising: Potential energy curves of highly excited states are more prone to error than lower ones since they often originate from the interaction between two open-shell excited-state atoms. Such interactions may lead to molecular electronic states which are very different from the reference ground state and thus demand an even more correlated approach than the coupled cluster method with single and double excitations that was employed in Ref. [17]. Moreover, the high density of electronic states
Indeed, the final vibrational distribution in the \( (1)^1\Pi_g \) state, plotted for various chirps in Fig. 2(b), shows a clear dependence on both sign and magnitude of the chirp parameter. The analysis is further supported by Fig. 2(c) which presents, for comparison, the final vibrational distribution in the \( (1)^1\Pi_g \) state, obtained within a reduced two-state model. It comprises only the \( X^1\Sigma_g^+ \) and \( (1)^3\Pi_g \) states rather than all the electronic states of the full model. The results of the two-state model differ both qualitatively and quantitatively from those of the full model and show, in particular, no dependence on the sign of the chirp. The chirp dependence in the full model can then be rationalized in terms of resonant Raman transitions between the \( (1)^3\Pi_g \) state and the higher lying \( u \)-states: The time dependence of the instantaneous frequency of the chirped pulse leads to an up (down) shift of the \( (1)^1\Pi_g \) vibrational distribution for negative (positive) chirp. The magnitude of the up- or down-shift depends on the absolute value of the chirp parameter. Down-shifting the \( (1)^1\Pi_g \) vibrational distribution results in an enhanced UV emission signal \( I_{UV} \) because it favors transitions into bound levels of the \( A^1\Sigma_u^+ \) state in the probed UV-emitting band, whereas an up-shifted \( (1)^3\Pi_g \) vibrational distribution is predominantly excited into dissociative states which do not contribute to the molecular emission signal. Our picture of a perturbative final probe photon is confirmed by comparing the calculated final vibrational distributions in the UV emitting states to the Franck-Condon projection of the final \( (1)^3\Pi_g \) distribution onto these states. The narrowing of the vibrational distribution due to the chirp, observed in both Fig. 2(b) and (c), is readily understood in terms of a competition between non-resonant Stark shifts and chirp. The chirp lowers the peak intensity and thus the Stark shift such that less power broadening of the vibrational distribution is induced by the chirped pulses as compared to the TL pulse. Figure 2(b) also indicates why a chirp rate of \( k = 0.015 \) ps\(^2\) is optimal: For even larger chirps, we do not observe a further down-shift of the \( (1)^3\Pi_g \) vibrational distribution. This is attributed to both the limited bandwidth of the pulse and the significantly reduced peak intensity for larger chirps. Thus the optimal chirp results from a competition between sufficient intensity for the Raman transitions and down-shifting of the vibrational distribution. This interpretation is also supported by the larger peak enhancement observed for the larger intensity in Fig. 1(b).

Our understanding of the control being facilitated by shaping the vibrational \( (1)^1\Pi_g \) distribution suggests that further enhancement of the PA signal should be possible by exploiting the \( (1)^3\Pi_g \) vibrational dynamics, in addition to the Raman transitions. To explore this possibility, we have experimentally carried out an automated closed-loop phase optimization using a learning algorithm \([6]\), with the measured PA enhancement relative to the TL pulse as the performance criterion. Each generation of
the learning algorithm contains 24 members (chromosomes), where each member is a spectral phase pattern applied to the pulse. The first generation of the optimization includes the five best linearly chirped pulses, with \( k = 0.004 \text{ ps} \) to \( 0.008 \text{ ps}^2 \), while all other members are random. Figure 3(a) shows the maximally obtained PA enhancement, achieved within each generation, as a function of the generation number. A fast increase of about 35% in the maximum enhancement is observed, from a value of 5.4 at the first generation to a value of about 7.4 after 130 generations. The two corresponding pulses, i.e., the best linearly chirped pulse and the optimized pulse, are shown in Fig. 3(b). While the optimization essentially keeps the positive linear chirp, the main change consists in a temporal splitting of the optimized pulse into two sub-pulses with a time delay of 130 fs. This time delay corresponds to the vibrational period of the \( (1)^1\Pi_g \) levels in the excitation region. It indicates that the optimized pulse utilizes the vibrational dynamics for improving the PA enhancement.

When testing the experimentally optimized pulse in our theoretical model, an enhancement of 7.1 is obtained, surprisingly close to the experimental value. Comparing the dynamics under the experimentally optimized pulse to that of the best linearly chirped pulse reveals the optimized pulse to populate a significantly broader vibrational band in the \( (1)^1\Pi_g \) state, with more population in the lower levels that can directly be excited by a one-photon transition into the probed UV-emitting band. The optimized pulse is thus shaped to enhance the transition probability in the resonant Raman transitions to the lower \( (1)^1\Pi_g \) levels. The role of coherent vibrational dynamics in the \( (1)^1\Pi_g \) state is further analyzed in Fig. 4 which displays the vibrational coherence and dynamics in the \( (1)^1\Pi_g \) state.

In summary, we observe strong-field coherent control of bond formation in the femtosecond photoassociation of thermally hot magnesium atoms using phase-shaped laser pulses. Our modeling from first principles has allowed us to identify a combination of Franck-Condon filtering in the free-to-bound non-resonant two-photon step with chirp-dependent resonant Raman transitions and coherent vibrational dynamics in an intermediate electronic state to be responsible for the control. Whereas the purpose of the FC filtering is mainly purification in order to allow the generation of molecular coherence, the Raman transitions and vibrational dynamics serve to realize phase control. Indeed, the quantum purity in the intermediate state and final UV-emitting states differ by only 25% for the experimentally optimal linear-chirp of \( k = 0.006 \text{ ps}^2 \). Our demonstration of coherent control of bond-making under thermal conditions points the way toward controlling transition probabilities and branching ratios to different target states. For photo-induced chemical reactions with several product channels, suitable target states would be those that serve as a gateway to a different product channel. A feasible route to the coherent control of photo-induced bimolecular chemical reactions is now open.
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In detail, the Hamiltonian in Eq. (12) of Ref. [17] has been augmented to include four additional states, \(1^3\Delta_g\) (dissociating into \(^1D + ^1S\) atoms), \((1)^1\Delta_u\) \((^1D + ^1S)\), \((2)^1\Sigma^+\) \((^3S + ^1S)\), and \((3)^1\Sigma_u^+\) \((^3P + ^3P)\). If not accounted for explicitly, these states cause resonances in the Stark shifts of the lower lying states.