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Communication: Transfer of more than half the population to a selected rovibrational state of H₂ by Stark-induced adiabatic Raman passage

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By using Stark-induced adiabatic Raman passage (SARP) with partially overlapping nanosecond pump (532 nm) and Stokes (683 nm) laser pulses, $73\% \pm 6\%$ of the initial ground vibrational state population of H₂ ($v = 0, J = 0$) is transferred to the single vibrationally excited eigenstate ($v = 1, J = 0$). In contrast to other Stark chirped Raman adiabatic passage techniques, SARP transfers population from the initial ground state to a vibrationally excited target state of the ground electronic surface without using an intermediate vibronic resonance within an upper electronic state. Parallel linearly polarized, co-propagating pump and Stokes laser pulses of respective durations 6 ns and 4.5 ns, are combined with a relative delay of ~4 ns before orthogonally intersecting the molecular beam of H₂. The pump and Stokes laser pulses have fluences of ~10 J/mm² and ~1 J/mm², respectively. The intense pump pulse generates the necessary sweeping of the Raman resonance frequency by ac (second-order) Stark shifting the rovibrational levels. As the frequency of the $v = 0 \rightarrow v = 1$ Raman transition is swept through resonance in the presence of the strong pump and the weaker delayed Stokes pulses, the population of ($v = 0, J = 0$) is coherently transferred via an adiabatic passage to ($v = 1, J = 0$). A quantitative measure of the population transferred to the target state is obtained from the depletion of the ground-state population using $2 + 1$ resonance enhanced multiphoton ionization (REMPI) in a time-of-flight mass spectrometer. The depletion is measured by comparing the REMPI signal of ($v = 0, J = 0$) at Raman resonance with that obtained when the Stokes pulse is detuned from the Stark-shifted Raman resonance. No depletion is observed with either the pump or the Stokes pulses alone, confirming that the measured depletion is indeed caused by the SARP-induced population transfer from the ground to the target state and not by the loss of molecules from photoionization or photodissociation. The two-photon resonant UV pulse used for REMPI detection is delayed by 20 ns with respect to the pump pulse to avoid the ac Stark shift originating from the pump and Stokes laser pulses. This experiment demonstrates the feasibility of preparing a large ensemble of isolated molecules in a preselected single quantum state without requiring an intermediate vibronic resonance. © *2013 American Institute of Physics.* [http://dx.doi.org/10.1063/1.4790402]

Molecular hydrogen, H₂, is the simplest of all neutral molecules, and studies of collisions of molecular hydrogen with other targets, such as H, F, or with well-defined surfaces, have provided detailed information on reaction dynamics and have served as a test of how well theory is able to predict the outcomes of various collisional processes.[1–5] Consequently, there is great interest in methods that could potentially be used to prepare a large number of isolated H₂ molecules in a single, metastable (v, J, M) quantum state; where v and J are the vibrational and rotational quantum numbers for the gas-phase molecule and M is the projection of the angular momentum vector, J, along a chosen symmetry axis of the collision system.[6–9] Although stimulated Raman adiabatic passage (STIRAP)[10] and Stark chirped two-photon, or Raman adiabatic passage (SCRAP),[11–16] might be thought of as appropriate methods for transferring population between rovibrational eigenstates of H₂, they require a suitably resonant, or near res-

onant intermediate vibronic state connecting the initial and final (target) vibrational levels of the ground electronic surface. For H₂, or any other molecule having a wide energy bandgap between the ground and excited electronic levels, STIRAP or SCRAP will require the use of vacuum ultraviolet (VUV) or extreme ultraviolet (XUV) pulses, making it difficult to realize in practice. Moreover, in the presence of an intermediate vibronic resonance, the short wavelength pulses may cause significant ionization or dissociation of the molecule. To achieve population transfer between two vibrational levels without requiring an intermediate vibronic resonance, we proposed the new technique of Stark-induced adiabatic Raman passage (SARP).[17] The temporal dynamics of SARP is described by a pure, two-level system represented by a 2×2 interaction Hamiltonian.[17,18] The Raman coupling between the two vibrational levels is mediated via distant off-resonant levels in upper electronic states and the Stark sweeping is accomplished by exploiting the off-resonant polarizabilities of the initial and target vibrational levels. It was proposed that by using a time-delayed sequence of off-resonant pump and Stokes laser pulses of unequal intensities, SARP can achieve a complete population

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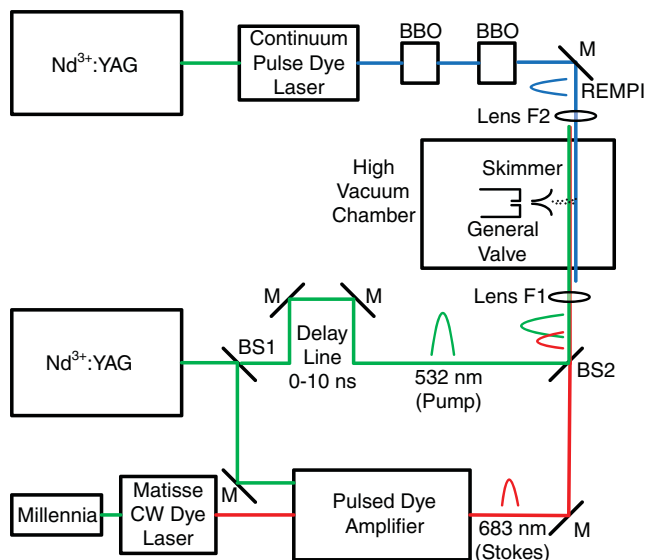
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FIG. 1. Schematic of the SARP experiment using partially overlapping pump and Stokes laser pulses. The 532 nm pulses (green) are harmonically generated by a seeded single-mode Nd^{3+}: YAG laser. After passing the delay line that is formed using high reflecting mirrors, M, the pump pulses are spatially overlapped with the Stokes pulses (red) from the dye laser at the dichroic beamsplitter, BS2. Then both laser pulses are focused to excite the molecular beam of H_2 in the vacuum chamber by lens F1 (focal length $\sim$40 cm). H_2 molecules in the ground and vibrationally excited states are selectively probed using 2 + 1 REMPI with deep UV pulses ($\sim$200 nm) counterpropagated through the vacuum chamber focused by lens F2 (focal length $\sim$20 cm). The H_2^+ ions are accelerated and detected by a time-of-flight mass spectrometer located perpendicular to the plane of the molecular beam and the laser pulses.

transfer between the ground and an excited rovibrational *M*-eigenstate.[17] This paper reports an experimental demonstration of SARP to selectively populate a single quantum state of the H_2 molecule.

To adiabatically transfer the population of the ground state ($v = 0$, $J = 0$) to an excited rovibrational state ($v = 1$, $J = 0$) of H_2, SARP combines a single-mode $\sim$200 mJ pump laser pulse at 532 nm with a time-delayed single-mode $\sim$20 mJ Stokes laser pulse at 683.6 nm on a dichroic beamsplitter before sending both pulses to excite a skimmed supersonic beam of H_2 molecules in a high vacuum ($\sim$10^{-7} Torr) chamber (see Fig. 1). The linearly polarized parallel pump and Stokes pulses have durations (intensity FWHM) of $\sim$6 ns and $\sim$4.5 ns, respectively, and they are focused to excite the molecular beam transversely. The single-mode Stokes laser pulse is derived from a pulsed dye amplifier (Newport Corp.) which is seeded by a frequency-stabilized, single-mode cw dye laser (Matisse DS, Newport Corp.). The single-mode Raman pump laser source at 532 nm is provided by the second harmonic of an injection-seeded Nd^{3+}: YAG laser (Continuum Lasers Inc.). A portion of the 532 nm beam is used to pump the pulsed dye amplifier generating the Stokes laser pulse. This arrangement allows the delay between the pump and the Stokes laser pulses to be varied using an optical delay line.

The central idea of SARP is described using a theoretical treatment based on the density matrix equations[17] describing the coherent interaction of the time-delayed pump and
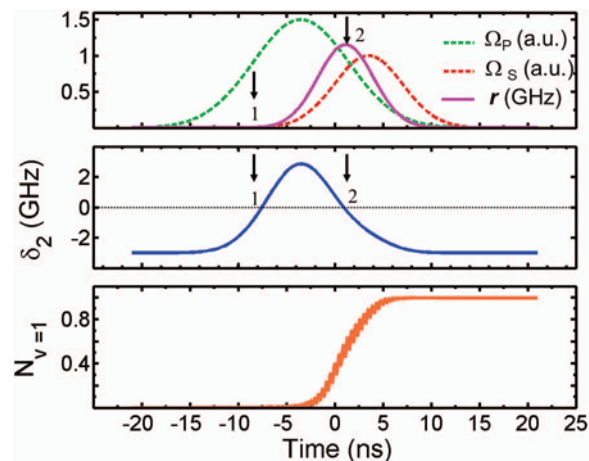

FIG. 2. Simulation of Stark-induced adiabatic Raman passage of H_2 ($v = 0$) $\rightarrow$ H_2 ($v = 1$) using temporally shifted but overlapping Gaussian pump Ω_P (top panel, dashed green), and Stokes Ω_S (dashed red) pulses. The top panel shows the Raman coupling term, $r \propto \Omega_P \Omega_S$ (purple). The middle panel shows the Stark-shifted Raman detuning, $\delta_2 = (\delta_0 - \delta_{ac})$ (blue). The bottom panel shows the fractional population transfer to $v = 1$ (orange).

Stokes laser pulses with the $v = 0$ and $v = 1$ vibrational levels (Fig. 2). An initial strong pump pulse (dashed green in the top panel of Fig. 2) causes an ac Stark-induced sweeping of the Raman resonance between the two rovibrational levels; the sweeping is described by a time-dependent Raman detuning, $\delta_2(t) = \delta_0 - \delta_{ac}(t)$ (blue in the middle panel of Fig. 2), where the quantity $\delta_0 = \omega_P - \omega_S - \omega_{10}$ is the zero-field static detuning, and $\delta_{ac}(t)$ is the dynamic Stark shift of the Raman resonance. In the presence of the intense pump pulse, δ_2 passes through resonance ($\delta_2 = 0$) twice, as shown by arrows 1 and 2 in Fig. 2. Population transfer between the vibrational levels takes place as the system passes through resonance ($\delta_2 = 0$) during the overlap of the pump and Stokes laser pulses. For the sequence of the pump and delayed Stokes laser pulses (top panel of Fig. 2), complete population transfer (orange in the bottom panel of Fig. 2) occurs at the second zero-crossing of δ_2, near the peak of the Raman interaction, $r(t) \propto \Omega_P \Omega_S$ (purple in the top panel of Fig. 2), which happens during the maximum overlap of the pump and Stokes pulses. Because the weaker Stokes pulse (dashed red in the top panel of Fig. 2) is delayed, in the absence of overlap between the pump and Stokes pulses, no Raman pumping occurs near the first zero-crossing of δ_2. Note that if the detuning, δ_2, crosses zero twice during the overlap of the pump and Stokes laser pulses, coherent population return[19,20] will result. The SARP process takes advantage of the relative intensities and the delay between the two pulses to ensure a unidirectional flow of population from the initial to the target state; that is, only one zero-crossing of δ_2 occurs during the maximum overlap of the pump and Stokes laser pulses. To prevent coherent population return in the overlap region of the pump and Stokes pulses, our simulations indicate that a relative delay of the order of the pulse duration and, a minimum pump to Stokes intensity ratio of four is required. If the rotational angular momentum quantum number of the prepared state is small, such as $J = 0$, or $J = 1$, or $J = 2$, then it is possible to populate just

one selected M state. For larger values of J, more M states are selected, but as described in detail in Ref. 17, all the M states are locked in phase.

H$_2$ molecules in the ground ($v = 0$, $J = 0$) or excited ($v = 1$, $J = 0$) rovibrational levels are selectively probed using $2 + 1$ resonance enhanced multiphoton ionization (REMPI) with UV pulses near 200 nm. The UV pulses are resonantly tuned to the Q branch of the appropriate two-photon H$_2$ E, F $^1\sum^+_g$ ($v' = 0$, $J' = J$) $- X$ $^1\sum^+_g$ ($v = 0, 1$, J) transition,[21] and the ions produced are collected by biased microchannel plates in a time-of-flight mass spectrometer (see Fig. 1). The tunable UV is obtained by using two different β-barium borate (BBO) crystals in sequence to generate the third harmonic of a tunable pulsed dye laser (ND 6000, Continuum Lasers Inc.). The pulsed dye laser is pumped by the second harmonic of a second Q-switched Nd^{3+}: YAG laser (Continuum Lasers Inc.). Relative to the pump and Stokes laser beams, the REMPI UV laser beam is more tightly focused and counterpropagated to also intersect the molecular beam transversely, as shown in Fig. 1. The REMPI signal is directly proportional to the number of molecules in the rovibrational level of the electronic ground state to which it is tuned. To avoid the strong ac Stark shift caused by the high intensity pump and Stokes laser pulses affecting the REMPI transition, the UV pulse is delayed by ∼20 ns relative to the pump pulse. The UV probe focus position on the molecular beam axis corresponds to the position of the maximum ($v = 1$, $J = 0$) REMPI signal.

Figures 3(a) and 3(b) present the experimental raw data of the REMPI signal from the excited H$_2$ ($v = 1$, $J = 0$) and ground H$_2$ ($v = 0$, $J = 0$) levels as a function of the Stokes laser frequency detuning for a pump to Stokes pulse delay of ∼4.2 ns. For the fixed pump wavelength near 532 nm, the Stokes laser frequency, which has a bandwidth ≤ 0.2 GHz, is scanned and the data are collected at intervals of 0.2 GHz. For each Stokes laser frequency the REMPI signal is integrated over the H$_2^+$ arrival time and averaged over 20 pulses. The standard deviation of the ion signal is $\leq 6\%$ for 20-pulse averaging. Because of the low temperature of the supersonic beam, there is almost no initial population in the $v = 1$ level, resulting in a nearly background-free REMPI signal from the excited $v = 1$ level; indeed, the signal disappears completely when the pump and Stokes pulses are detuned from the Raman resonance. Its magnitude does not permit the abso-
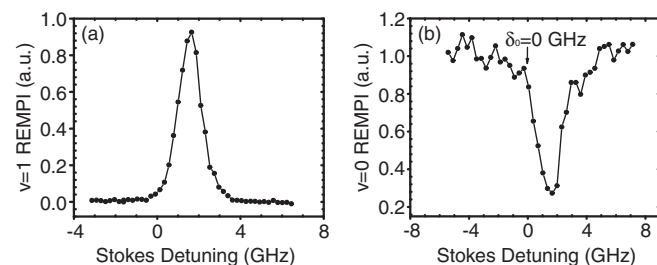
lute extent of population transfer to be determined without calibration. However, a direct and quantitative measurement of population transfer is obtained from the decrease in the $2 + 1$ REMPI signal arising from the depletion of the $v = 0$ ground state caused by the ($v = 0$, $J = 0$) $\rightarrow$ ($v = 1$, $J = 0$) Raman excitation. A maximum population transfer of 73% $\pm 6\%$ is measured from the depletion of the $2 + 1$ REMPI signal shown in Fig. 3(b).

Note that the depletion is measured by comparing the $2 + 1$ REMPI signal of the ($v = 0$, $J = 0$) ground state at Raman resonance with that obtained when the pump and Stokes pulses are detuned from the Raman resonance. This methodology, therefore, takes into account all other off-resonant contributions (including any potential loss from multiphoton ionization and molecular dissociation), and correctly measures the fractional population transfer, given by the depletion, that arises exclusively from the Raman resonance. Also, no depletion is observed with either the pump or the Stokes pulses alone, confirming that the observed depletion is indeed caused by SARP-induced population transfer to the target state.

Although the demonstration of SARP to prepare a single vibrationally excited M-eigenstate of the H$_2$ molecule with 73% population of the initial ground vibrational state is a significant achievement and opens many possibilities for fundamental stereodynamical studies, it falls short of the theoretically predicted 100% population transfer. The main limiting factor in the experiment is related to the limited collimation of our molecular beam. With the current apparatus, the width of our molecular beam is much wider than the Rayleigh range (4–5 mm) of the focused pump and Stokes laser beams, which causes non-uniform SARP excitation of the molecular beam along the direction of propagation of the pump and Stokes laser beams. As a result, the population transfer, as measured by the depletion of REMPI signal of the ($v = 0$, $J = 0$) ground state, depends upon the location of the UV probe beam focus relative to the pump and Stokes laser beams within the vacuum chamber. The UV probe beam is tuned to the REMPI line center and is focused close to the SARP excitation volume with an estimated spot size of 20 μm. After a delay of ∼20 ns between the pump and probe, the maximum depletion signal is observed only when the focused spot of the REMPI UV beam is within, or in the closest proximity to, the SARP excitation volume. Moving the UV focus further down the molecular beam reduces the depletion signal significantly, suggesting that our molecular beam apparatus does not have the necessary collimation to ensure that we are exclusively probing molecules that only pass through the tightly focused interaction volume of the pump and Stokes laser beams. We suggest that this fact contributes strongly to why we do not observe the higher population transfer predicted from theory.

Because we are pumping a relatively wide molecular beam, and also because of the unknown beam parameters of the pump and Stokes laser beams which are focused differently by a slightly dispersive fused silica lens, it is difficult to know the exact fluences over the interaction length of the pump and Stokes laser beams. A crude measurement of the laser beam profile using a 5 μm diameter iris and a photodiode shows that at the focus, the Stokes beam has a diameter of ∼120 μm, whereas the pump beam has an

FIG. 3. The $2 + 1$ REMPI signal (a.u.) from the Q branch E, $F^1\Sigma^+_g$($v' = 0$, $J' = J$) $- X^1\Sigma^+_g$($v = 0, 1$, J) transition versus the Stokes laser frequency detuning (GHz) from resonance (438 538.9 GHz) for a relative delay $\tau_D = 4.2$ ns between the pump and Stokes laser pulses. The REMPI UV light is polarized parallel to the pump and Stokes laser fields. (a) The $2 + 1$ REMPI signal from the H$_2$ ($v = 1$, $J = 0$) state and (b) the $2 + 1$ REMPI signal from the H$_2$ ($v = 0$, $J = 0$) ground state.

elliptical shape with the major and minor axes $\sim$120 μm and 40 μm, respectively. The direction of the molecular beam coincides with the minor axis of the elliptical pump beam. These beam parameters can be used to estimate the approximate pump and Stokes fluences in excess of 10 J/mm^2 and 1 J/mm^2, respectively, which satisfies the threshold condition for adiabatic following[22] near the focus. The observed spectral widths of the $v = 1$ and $v = 0$ REMPI signals in Figs. 3(a) and 3(b) are consistent with an ac Stark broadening rate[23] of $\sim$23 MHz/GW/cm^2 for the Q(0) Raman transition of H$_2$.

We note that, even though the molecular beam is poorly collimated with an estimated angular half width of $\sim$100 mrad, the residual Doppler width of $\sim$200 MHz for the Raman transition is considerably less than the SARP linewidth of $\sim$2 GHz. The SARP spectral width originates from the dynamic Stark-shift of the Raman transition. Consequently, the entire velocity distribution perpendicular to the axis of the molecular beam is uniformly pumped.

To confirm that the population is transferred to a single M-state via a coherent adiabatic Raman passage, we recorded the 2 + 1 REMPI signal for $v = 0$ as a function of the Stokes laser frequency detuning for two relative delays τ_D between the pump and the Stokes laser pulses. Figure 4 compares the experimental SARP-induced population transfer (Fig. 4(a)) to a theoretical simulation of an ideal adiabatic Raman passage (Fig. 4(b)) as a function of the Stokes laser frequency detuning for relative delays $\tau_D = 0$ ns (completely overlapping) and $\tau_D = 4.2$ ns (partially overlapping) between the pump and Stokes laser pulses. The simulation in Fig. 4(b) assumes Gaussian pump and Stokes pulses with durations and fluences comparable to those of our experiment. For zero delay, shown in Fig. 4(b), the population exhibits Rabi oscillations in frequency space. Experimentally, however, these oscillations are averaged out and the smooth spectrum in Fig. 4(a) is observed. Both experiment (Fig. 4(a)) and theory (Fig. 4(b)) show a spectral broadening for the large (4.2 ns) relative delay—which is a hallmark of coherent population transfer via Stark-induced adiabatic Raman passage. For values of the delay close to zero, population transfer is sensitive to both the frequencies and the fluences of the pump and Stokes laser pulses, whereas, a large and reproducible population transfer is realized for the large relative delay. The qualitative agreement between experiment and theory confirms that the population transfer is achieved by a coherent
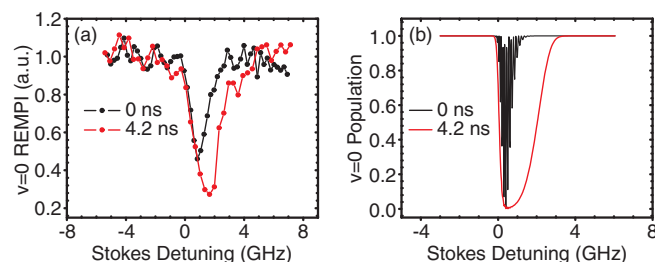
adiabatic passage. As the delay between the pump and Stokes laser pulses is varied over a few discrete values around 0 ns, 4 ns, and 7 ns, population transfer is found to reach a maximum near 4 ns.

Using SARP with partially overlapping pump (532 nm) and Stokes (699 nm) pulses we have also measured a 60% $\pm$ 6% transfer of the ($v = 0$, $J = 0$) ground state population to the H$_2$ ($v = 1$, $J = 2$, $M = 0$) state. These experimental results are a significant improvement over the transfer of only a few percent which has been previously recorded[9,24] for isolated H$_2$ or D$_2$ molecules under collision-free conditions. These results could be improved by using a molecular beam apparatus with better molecular beam collimation. We believe that we have demonstrated a novel Raman adiabatic passage technique that is able to prepare a single quantum state of H$_2$ or D$_2$ molecules with a significant fraction of the ground state population. Because SARP does not use a near resonant intermediate excited electronic state to couple the two metastable vibrational levels of the ground electronic state, it is more versatile than other adiabatic Raman passage techniques, and thus provides a practical way to prepare a large ensemble of molecules in a single quantum state.

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FIG. 4. SARP-induced population transfer (a) experimental REMPI signal and (b) theoretical fractional population in $v = 0$, $J = 0$ state for two different relative delays $\tau_D = 0$, and 4.2 ns between the 6 ns (intensity FWHM) pump and 4.5 ns Stokes laser pulses. The pulse energies are nearly the same as in Fig. 3.