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Efficient Coherent Population Transfer of D_2 Molecules by Stark-induced Adiabatic Raman Passage

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Preparation of a high flux of hydrogen molecules in a specific vibrationally excited state is the major prerequisite and challenge in scattering experiments that use vibrationally excited hydrogen molecules as the target. The widely used scheme of stimulated Raman pumping suffers from coherent population return which severely limits the excitation efficiency. Recently we successfully transferred D_2 molecules in the molecular beam from (v=0, J=0) to (v=1, J=0) level, with the scheme of Stark-induced adiabatic Raman passage. As high as 75% of the excitation efficiency was achieved. This excitation technique promise to be a unique tool for crossed beam and beam-surface scattering experiments which aim to reveal the role of vibrational excitation of hydrogen molecules in the chemical reaction.

Key words: Stark-induced adiabatic Raman passage, D_2, Vibrational excitation, Molecular beam

I. INTRODUCTION

Molecular hydrogen is very special for chemists because of its ubiquitous presence in numerous important reactions and the simplicity for theoretical simulations. In the past decades, scattering experiments, especially crossed beam experiments of molecular hydrogen with free radicals such as H [1, 2], F [3, 4], and OH [5], played a pivot role in understanding the nature of chemical reactions. In these reactions, the vibration of molecular hydrogen may have pronounced effects, because H−H bond is the bond to be broken.

Preparation of a large flux of the hydrogen molecule in a specified vibrational level is the major prerequisite and challenge to study the effect of vibrational excitation on reactivity. Molecular hydrogen does not possess a dipole moment, therefore direct infrared (IR) absorption cannot be applied to vibrationally excite it. The scheme of stimulated Raman pumping (SRP) is widely used to prepare vibrational excitation of nonpolar molecules in the molecular beam in scattering experiments, such as the "photoloc" experiments [6−8] and beam-surface scattering experiments [9]. However, under molecular beam condition the excitation efficiency is severely limited by coherent population return [10, 11]. The poor performance of the SRP scheme is the bottleneck for many scattering experiments, especially crossed beam experiments.

To circumvent this limitation, Zare and Mukherjee proposed the scheme of Stark-induced adiabatic Raman passage (SARP) [12], similar to the scheme of SCARP proposed by Bergmann and co-workers [13, 14]. SARP is an important extension of adiabatic passage technique [15, 16] to Raman-active modes. The numerical simulation suggests that almost complete population transfer of H_2 from the vibrationally ground state to the vibrationally excited state is possible. This scheme takes advantage of laser-induced Stark shifts to drive an adiabatic population transfer between two vibrational levels. The frequency difference of the pump and Stokes laser is tuned closed to, but not exactly equals to the zero-field energy difference of the ground and rovibrationally excited levels. The pump and Stokes pulses are temporally displaced and of unequal intensities. The stronger pulse induces the dynamical Stark shift and sweeps the molecular energy level through resonance, so an adiabatic evolution takes place and the ground state population is transferred to the upper state [16]. The zero-crossing happens only once during the course of Raman interaction, so the CPR can be prevented.

SARP is expected to be a technique of high efficiency, quantum-state selectivity and robustness. It should be noted that a resonant intermediate level is not required in the scheme, so the vibrational excitation can be achieved with immediately available lasers in the visible spectral region. Attracted by these features, we attempted to prepare molecular hydrogen and its isotopic variants in the vibrationally excited states with SARP

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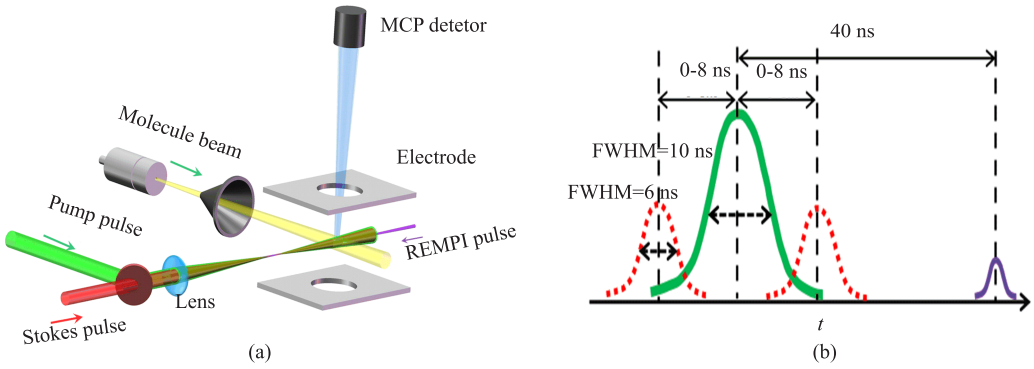

FIG. 1 (a) Scheme for SARP pumping and REMPI detection of D_2 molecules. The pump pulse and Stokes pulse are collinearly combined by a dichroic mirror and perpendicularly intersected with the D_2 molecular beam. A counterpropagating REMPI laser is spatially overlapped with the SARP interaction region. D_2 molecules in the SARP interaction region is vibrationally excited by the pump and Stokes pulses and then probed by REMPI pulse. (b) The timing sequence of the pump, Stokes and REMPI pulse.

scheme. In this work, we study the first experimental demonstration of highly efficient population transfer of D_2 molecule with this scheme.

II. EXPERIMENTAL SETUP

A pulsed molecular beam of pure D_2 (Cambridge Isotope Laboratories, Inc., 99.8% purity) was generated from an Even-Lavie valve, and intersected at right angle by three laser beams, at the wavelengths of 532, 633, and 201−210 nm, respectively. The 532 and 633 nm laser acted as SARP lasers to vibrationally excite the D_2 molecules from (v=0, J=0) level to (v=1, J=0) level. The 201−210 nm laser was used to measure the quantum-state distribution of the D_2 beam with the scheme of resonance-enhanced multiphoton ionization (REMPI) [17]. The REMPI laser was delayed 40 ns relative to the SARP laser, in order to prevent SARP lasers from interfering the REMPI detection [10]. The experimental schematic is shown in Fig.1.

The SARP laser system consists of two injection-seeded Nd:YAG lasers and a home-built narrow-bandwidth optical parameter oscillator/amplifier system (OPO/OPA). The OPO/OPA system was similar to the design of Wodtke and coworkers [18], but with an additional OPA stage to increase the output energy. Pumped by 180 mJ of the second harmonic of injection-seeded Nd:YAG laser I (Continuum Inc., PL8000 DLS), it could generate near Fourier-transform limited bandwidth laser pulses at 633 nm, which acted as Stokes pulse with typical pulse energies of 25 mJ and a pulse duration of about 6 ns (FWHM). About 300 mJ of 532-nm, single-longitudinal-mode laser with a pulse duration of about 8 ns (FWHM), acting as the pump pulse, was generated from frequency doubling of injection-seeded Nd:YAG laser II (Continuum Inc. PR8000 OPO). Stokes laser and the pump laser were combined collinearly with a dichroic mirror and then focused on the molecular beam with a lens of 300 mm focal length. A lens of 1500 mm focal length was used for the dispersion compensation of Stokes laser. The diameters of both lasers at the interaction region were reduced to about 0.25 mm. Their wavelengths were measured by a high resolution wavemeter (HighFinesse GmbH, WS7) and sent to a computer, which stabilized the energy difference of the pump and Stokes photons to within 0.002 cm^{-1}. Both of the pump and Stokes laser were vertically polarized.

The third Nd:YAG laser (Spectra Physics, Pro-290) pumped a tunable dye laser (Sirah GmbH, PESC-G-24) operating with DCM dye in ethanol solution. More than 15 mJ of fundamental, at the wavelength of 603−630 nm, was generated from the dye laser and then converted to the second harmonic by a potassium dideuterium phosphate crystal (DKDP, Castech Inc., θ=53°). The residual fundamental was mixed with the second harmonic in a β-Barium Borate crystal (β-BBO, Castech Inc., θ=73°) to yield more than 1 mJ of the third harmonic at the wavelength of 201−210 nm. The third harmonic, acting as the REMPI laser, was separated from the fundamental and the second harmonic by an equilateral dispersive prism, and guided to the vacuum chamber by right angle prisms. A 300 mm-lens was used to reduce the REMPI laser to a spot size of about 0.1 mm diameter. The REMPI laser was spatially overlapped with the SARP excitation region. In order to avoid saturation of the detection, the REMPI laser was attenuated to about 0.67 mJ. A schematic diagram for the experimental setup is shown in Fig.2.

III. RESULTS AND DISCUSSION

With the experimental setup mentioned above, we attempted to transfer D_2 from (v=0, J=0) to (v=1, J=0) using SARP scheme. The energy difference of the pump and Stokes photons was fixed at $\Delta\omega$=2993.605 cm^{-1}

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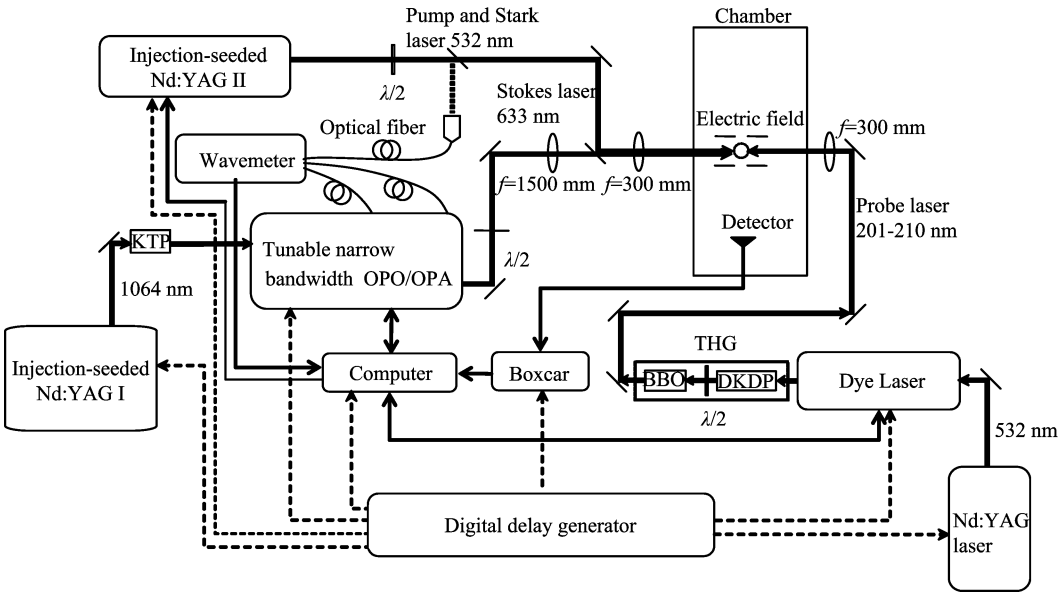

FIG. 2 A schematic diagram for the experimental setup.

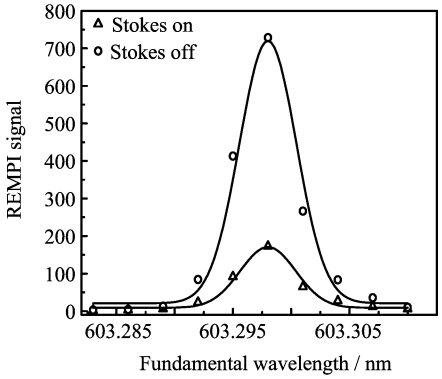

FIG. 3 REMPI spectral peaks of D_2(v=0, J=0) level, with SARP laser on and off, respectively. The 75% depletion of the peak area indicates that 75% population of the D_2(v=0, J=0) is promoted to (v=1, J=0) level by SARP pulses.

(λ_p=532.21636 nm, and λ_p=633.08184 nm). Stokes pulse was 4 ns later than the pump pulse. The REMPI spectral peak of D_2(v=0, J=0) was recorded, as shown in Fig.3. When both the pump and Stokes laser were applied on the D_2 beam, the REMPI spectral peak of D_2(v=0, J=0) was significantly depleted, and the REMPI spectral peak of D_2(v=1, J=0) could be observed. If we blocked Stokes laser, and allowed only the pump laser to interact with the D_2 beam, neither the depletion of (v=0, J=0) REMPI peak nor any REMPI signal from (v=1, J=0) was observed. This indicated a considerable portion of (v=0, J=0) population had been transferred to (v=1, J=0) level under the interaction of the pump and Stokes lasers. The absolute excitation efficiency was obtained by calculating the difference of the peak areas with Stokes laser on and off. With Stokes laser on, 75% of the peak area was depleted compared to the situation with Stokes laser off. This indicated that 75% population of the ground state (v=0, J=0) had been transferred to the first vibrationally excited state (v=1, J=0). It should be noted that REMPI pulse and SARP pulses were fully temporally separated, so REMPI detection was not interfered by the dynamical Stark shift induced by SARP lasers [10]. A major difference of the SRP and SARP is the upper limit of the excitation efficiency. In SRP scheme, no more than 50% of the ground state population can be promoted to the vibrationally excited state. While the SARP theory predicted that excitation efficiency more than 50% is possible. So 75% depletion of the ground state population indicates that the pumping process in this experiment is truly a SARP process.

In order to reveal the relation between the time delay t and the excitation efficiency, we fixed the energy difference of the pump and Stokes photons at $\Delta\omega$=2993.605 cm^{-1}, and then measured the excitation efficiency at different time delay with 2 ns interval. Two methods were used to measure the excitation efficiency. By measuring the difference of areas of the (v=0, J=0) REMPI spectral peaks with Stokes laser on and off, we obtained the absolute excitation efficiency. Or, by measuring the integral area of the (v=1, J=0) REMPI spectral peak, we obtained the relative excitation efficiency, which could be scaled to the absolute excitation efficiency assuming the excitation efficiency at t=4 ns is the same. With both methods, we got very similar M-shape curves, as shown in Fig.4, indicating these methods probed exactly the same process. At $t<-8$ ns and $t>8$ ns, the excitation efficiency was very low, approaching zero when the pump and Stokes pulses were further temporally separated. When the temporal sep-

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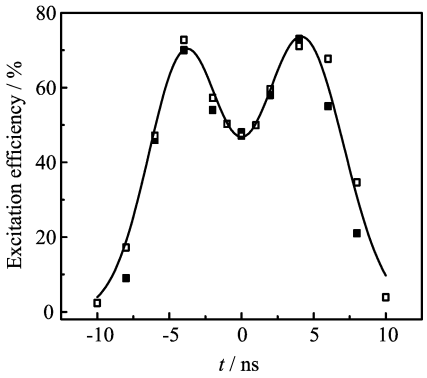

FIG. 4 The time-delay t dependence of the excitation efficiency. The (v=0, J=0) depletion (solid square) corresponds the absolute excitation efficiency. The (v=1, J=0) signal (open square) is a measurement of the relative excitation efficiency, which is scaled down for comparison with the absolution excitation efficiency. The minimum at t=0 ns indicates that a fraction of the excited population returns to the ground state when two SARP pulses are fully overlapped in time.

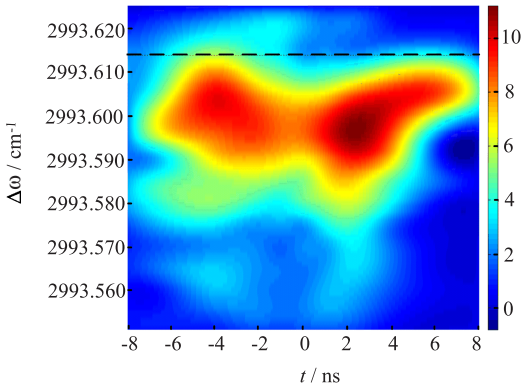

FIG. 5 The relative excitation efficiency was measured as the integral area of D_2(v=1, J=0) REMPI spectral peak. A dashed line at $\Delta\omega$=2993.615 cm^{-1} indicates the position of $Q(0)$ Raman transition in zero electric field.

aration between the two pulses decreased, the excitation efficiency significantly increased and two maximum appeared at t=−4 ns and t=4 ns, respectively. However, when the pump and Stokes pulses became temporally closer, the excitation efficiency decreased again and a local minimum occurred at t=0 ns. The M-shape curved is consistent with SARP theory, which predicted two maximal excitation efficiency appears at appropriate time delay, and a local minimum appears when the pump and Stokes pulse are perfectly overlapped in time. Being a major difference from SRP process, the M-shape curve demonstrated a SARP process indeed took place in this experiment.

We also investigated the effect of detuning on SARP process. The relative excitation efficiency is measured as the integral area of D_2(v=1, J=0) REMPI spectral peak, with 2 ns interval in time-delay from −8 ns to 8 ns, and detuning with a step-size of 0.005 cm^{-1} from 2993.550 cm^{-1} to 2993.625 cm^{-1}. The original data points were interpolated to produce the 3-dimension contour, as showed in Fig.5. The region surrounded by the yellow lines exhibits as a V-shape plateau. In this region, the excitation efficiency is greater than 50%. The reported $Q(0)$ Raman line position in zero electric field is $\Delta\omega$=2993.617 cm^{-1} [19]. So the effective excitation takes place blow $\Delta\omega$=2993.615 cm^{-1} (the dashed line in Fig.5), as expected from the direction of dynamic Stark shift. The 3-dimentioan contour is not symmetric with respect to t=0 ns. The excitation efficiency on the right side is higher than that on the left side. We believed this asymmetricity is the result of the deviation of the temporal profile of Stokes pulse from a perfect Gaussian profile. Stokes pulses generated from our OPO/OPA system feature a fast leading edge and a slow trailing edge. If Stokes pulse is applied prior to the pump pulse, the D_2 molecules will be transferred to (v=1, J=0) level at the rising edge of the pump pulse and a portion of the excited population will return to (v=0, J=0) level at the falling edge. If Stokes pulse is subsequent to the pump pulse, the ground population will be promoted to the upper state at the trailing edge of the pump pulse, and then it will not be transferred back to the ground state by SARP lasers. For efficient excitation, $\Delta\omega$ should be kept in the range of 2993.585 cm^{-1} to 2993.610 cm^{-1}, suggesting that the long-term drift of the energy difference of the pump and Stokes photons must be monitored and stabilized with very high accuracy.

IV. CONCLUSION

We have demonstrated a novel technique to selectively transfer D_2 molecules to a specific vibrationally excited state with efficiency as high as 75%, with the scheme of SARP. Both time delay and frequency detuning have profound effects on the excitation efficiency. This technique promise to be a unique tool for scattering experiments with vibrationally excited H_2, HD, D_2, which will provide in-depth insights to the role of H−H bond in chemical reactions.

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