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Preparation of a selected high vibrational energy level of isolated molecules

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Stark induced adiabatic Raman passage (SARP) allows us to prepare an appreciable concentration of isolated molecules in a specific, high-lying vibrational level. The process has general applicability, and, as a demonstration, we transfer nearly 100 percent of the HD ($v = 0, J = 0$) in a supersonically expanded molecular beam of HD molecules to HD ($v = 4, J = 0$). This is achieved with a sequence of partially overlapping nanosecond pump (355 nm) and Stokes (680 nm) single-mode laser pulses of unequal intensities. By comparing our experimental data with our theoretical calculations, we are able to draw two important conclusions: (1) using SARP a large population ($>10^{10}$ molecules per laser pulse) is prepared in the ($v = 4, J = 0$) level of HD and (2) the polarizability $\alpha_{00,40}$ ($\cong 0.6 \times 10^{-41}$ C m² V⁻¹) for the ($v = 0, J = 0$) to ($v = 4, J = 0$) Raman overtone transition is only about five times smaller than $\alpha_{00,10}$ for the ($v = 0, J = 0$) to ($v = 1, J = 0$) fundamental Raman transition. Moreover, the SARP process selects a specific rotational level in the vibrational manifold and can prepare one or a phased linear combination of magnetic sublevels (M states) within the selected vibrational-rotational level. This capability of preparing selected, highly excited vibrational levels of molecules under collision-free conditions opens new opportunities for fundamental scattering experiments. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4964938>]

INTRODUCTION

A long-sought-after goal is to prepare molecules in specific, high-lying vibrational levels so that their scattering dynamics can be studied in detail. This objective has proven to be difficult to attain by straightforward optical excitation schemes. The problem would seem to be that while the fundamental ($v = 0 \rightarrow v = 1$) direct vibrational transitions of polar molecules can have some strength, the overtone transitions ($v = 0 \rightarrow v \geq 2$) are considered to be so weak that this goal cannot be practically realized. For example, Lehmann¹ examined in detail overtone intensities and stated, “The empirical rule of thumb, that the first overtone is 100 times weaker than the fundamental, and each successive overtone a factor of 10 weaker still works surprisingly well as an intensity estimate across a large number of molecules.”

This same reduction in coupling might be thought to apply to overtones of Raman transitions, but, as will be shown here, this belief is not correct. We are able to achieve a nearly complete transfer of population between one vibrational level and a higher one through a coherent process involving adiabatic following, which we call Stark induced adiabatic Raman passage (SARP).² In previous work we used SARP to transfer nearly 100% of the population in H₂ ($v = 0, J = 0$) to H₂ ($v = 1, J = 0$) in a beam of molecular hydrogen (H₂).³⁻⁵ We report here the nearly complete population transfer of HD ($v = 0, J = 0$) to HD ($v = 4, J = 0$) in a supersonically expanded beam of pure HD, which shows the generality of this method to prepare isolated molecules, polar and nonpolar, in specific quantum states of high internal energy. In what follows, we describe in detail the specific preparation of HD ($v = 4$), but the reader should keep in mind that other molecules can be prepared in other high-lying vibrational levels with the availability of suitable laser sources. Besides

the related adiabatic passage process called stimulated Raman adiabatic passage (STIRAP),⁶ to our knowledge, SARP is currently the only technique capable of preparing single highly excited states of molecules with large enough populations to be useful in scattering or other fundamental experiments.

ADIABATIC PREPARATION OF A SELECTED HIGHLY EXCITED VIBRATIONAL LEVEL

Previously, we have introduced SARP, which is a technique that takes advantage of the dynamic Stark shift to adiabatically transfer population from the initial to the target state using a sequence of partially overlapping nanosecond pump and Stokes single-mode laser pulses of unequal intensities. A detailed description of SARP can be found elsewhere.² As mentioned before, we have demonstrated SARP's ability to pump H₂ molecules from the ground vibrational to the first excited vibrational state with large transfer.³⁻⁵ Yang and co-workers have demonstrated HD $v = 1$ excitation using SARP.⁷ These results are not surprising because, traditionally, stimulated Raman pumping is utilized to reach the $v = 1$ level of H₂ and other homonuclear molecules. However, because of the weaker Raman polarizability for the overtone transitions, a much higher laser intensity is required to Raman pump a higher vibrational level ($\Delta v > 1$). At this high laser intensity, the dynamic Stark shift becomes substantial, destroying the two-photon Raman resonant condition and resulting in negligible or no detectable excitation.

SARP overcomes this problem by transferring population via adiabatic passage, which takes place in the presence of a time-dependent shift or chirping of the vibrational levels by the dynamic Stark effect. Briefly, the optical intensity

of the stronger pulse dynamically sweeps the detuning of the Raman transition frequency generating two crossings through the resonance during optical excitation. By controlling the relative delay between the pump and Stokes pulses, a significant Raman coupling is realized only at one of the two crossings (commonly known as the avoided crossing). In these experiments, we demonstrate that by separating the pump and Stokes pulses in time, we have ensured the unidirectional flow of population through a single crossing of the Raman resonance, which successfully achieves population transfer from the ground to the fourth vibrational state of the HD molecule.

SARP achieves complete population transfer from the initial to the target state via the avoided crossing only when the adiabatic following condition is satisfied. The adiabatic following condition, also known as the Landau-Zener condition, can be expressed mathematically as $d\Delta/dt \leq 2\pi\Omega^2$ where Δ is the time-dependent detuning of the two-photon resonance and Ω is the two-photon Rabi frequency for the selected Raman transition between the initial and final vibrational levels within the ground electronic state of the molecule. $\Omega = (r_{12}/\hbar)E_P E_S^*$, where E_P and E_S are the electric fields associated with the pump and Stokes laser pulses. The two-photon Raman coupling coefficient r_{12} is given by²

$$r_{12} = \frac{1}{\hbar} \sum_k \mu_{1k} \mu_{k2} \left[\frac{1}{(\omega_{k1} - \omega_P)} + \frac{1}{(\omega_{k1} + \omega_S)} \right],$$

where 1 and 2 represent the initial ($v = 0, J$) and final ($v' > 0, J'$) rovibrational levels within the ground electronic state of the molecule satisfying the two-photon resonant condition: $\omega_{21} \approx \omega_P - \omega_S$. Here k represents the vibronic levels belonging to the manifold of excited electronic states, and μ_{1k} and μ_{k2} are the transition dipole moment matrix elements between the ground vibrational level and the vibronic level k , and the vibronic level k and the target vibrational level, respectively. The values of the transition dipole moments depend upon the different overlaps of the vibrational wavefunctions of the involved electronic surfaces. This fact implies that the value of r_{12} is a function of the ground and excited electronic surfaces which is demonstrated by the theoretical calculations of Chelkowski and Bandrauk⁸ showing that r_{12} for H_2 oscillates as a function of the target vibrational level. r_{12} can be recognized as the Raman transition polarizability $\alpha_{vJ, v'J'}(\omega_{21}; \omega_P, \omega_S)$,⁹⁻¹¹ which is responsible for inducing a dipole moment at the Stokes frequency ω_S via the interaction of the pump electric field at frequency ω_P with the vibrating molecule. The Landau-Zener condition tells us that for a given frequency sweeping rate (i.e., for a given rate of change of laser pulse intensity in time), a certain Rabi frequency is required to achieve population transfer.

By optimizing both the relative powers and the delay between our pump and Stokes pulses, we have exploited adiabatic following to achieve population transfer with SARP. Based on our estimate of the Raman coupling for the $v = 0$ to $v = 4$ transition in H_2 , we predicted that SARP would be able to achieve complete population transfer. In the absence of a suitable laser source at the Stokes frequency for this transition, we have instead chosen to excite HD ($v = 4$) for which laser light at the Stokes frequency is currently available in our laboratory.

By comparing experimental data with detailed theoretical simulations, we draw two important conclusions. First, using SARP we are able to transfer a large fraction of the HD ($v = 0, J = 0$) population to the HD ($v = 4, J = 0$) state. Second, the Raman polarizability for the HD $v = 0$ to $v = 4$ transition is approximately 20% of the value of the polarizability for the H_2 $v = 0$ to $v = 1$ transition.

EXPERIMENT

A supersonic beam of HD molecules within a high vacuum reaction chamber is excited using a single-mode ~ 9.5 ns pump pulse (~ 150 mJ) at 355 nm and a single-mode, partially overlapping ~ 5 ns Stokes pulse (~ 20 mJ) at 680 nm. The pump laser pulse is obtained from the third harmonic of an injection-locked, Q-switched Nd^{3+} :YAG laser (PRO-290, Spectra Physics). The Stokes pulse at 680 nm is derived from a pulsed dye amplifier (PrecisionScan, Sirah), which is seeded by a frequency stabilized ring dye laser (Matisse, Sirah). A delay of 3-10 ns is introduced between the pump and Stokes laser pulses using a variable optical delay line.

The delayed Stokes laser pulse is combined with the pump pulse on a dichroic beam splitter before both beams are focused on the molecular beam within the reaction chamber using a 40 cm focal length lens. A detailed description of our differentially pumped high vacuum chamber is available elsewhere.¹² The position of the 40 cm focal length lens is adjusted to bring the focus of the 680 nm Stokes beam within the center of a 2-3 mm wide supersonic beam of HD molecules. To avoid ionization of the molecular beam by the strong pump laser pulse at 355 nm, the focus of the pump beam is kept approximately 1 cm away from the center of the molecular beam. This arrangement enables a better overlap of the pump and Stokes laser beams within the molecular beam. To optimize the SARP excitation signal, the divergence of the pump and Stokes beams is adjusted independently using two beam expanders in their respective beam paths.

The excited HD molecules in the ($v = 4, J = 0$) level within the ground HD X $^1\Sigma_g^+$ electronic state are probed using the (2 + 1) resonance enhanced multiphoton ionization (REMPI) transition via the two-photon resonant E,F $^1\Sigma_g^+(v' = 0, J = 0)$ intermediate level with tunable UV pulses at 233.033 nm (vac). The 233 nm UV pulses are generated from the third harmonic of a tunable pulsed dye laser in two stages using two α -BBO crystals. The REMPI generated ions from the selected HD ($v = 4, J = 0$) level are detected on a pair of multichannel plates at the end of a flight tube. To avoid Stark shifting the (2 + 1) REMPI signal from the pump and Stokes pulses and to discriminate against ions generated by the 355 nm pump pulse, the probe UV pulse at 233 nm is delayed by 400 ns relative to the pump and Stokes pulses. The delay of 400 ns corresponds to a displacement of 0.9 mm downstream along the flight of the molecular beam. The (2 + 1) REMPI signal is directly proportional to the population of SARP excited HD ($v = 4, J = 0$) molecules within the X $^1\Sigma_g^+$ ground electronic state.

Figure 1 shows the REMPI signal from HD ($v = 4$) level as a function of the Stokes detuning for four different pump

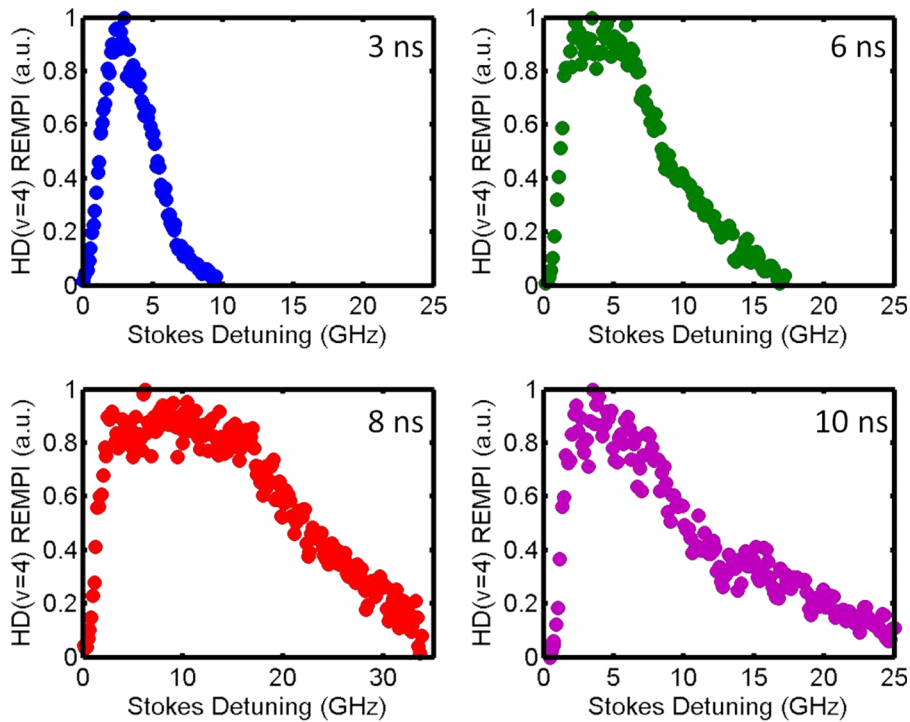


FIG. 1. Experimental (2+1) REMPI signal from SARP excited $X^1\Sigma_g^+$ HD ($v=4, J=0$) state as a function of Stokes frequency detuning for the pump to Stokes delays of 3 ns, 6 ns, 8 ns, and 10 ns. Pump fluence is approximately 12 J/mm^2 and Stokes fluence is approximately 1.3 J/mm^2 .

to Stokes delays of 3-10 ns. For the data in Fig. 1, the pump and Stokes fluences are held at $\sim 12 \text{ J/mm}^2$ and $\sim 1.3 \text{ J/mm}^2$, respectively. These pump and Stokes fluences are estimated using approximate beam spot sizes for the pump and Stokes lasers within the molecular beam. Figure 1 shows that the frequency bandwidth of SARP excited population transfer increases remarkably as the pump to Stokes delay increases from 3 ns to 8 ns and then decreases as the delay increases to 10 ns. This behavior might appear to be counter-intuitive because it would seem that increasing the delay between the

pump and Stokes pulses should result in an overall reduction in Raman driving force, resulting in decreased bandwidth. However, below, we give an intuitive explanation of how this bandwidth trend is caused by the adiabatic nature of SARP. In addition, as we will show later, our theoretical models indicate that this bandwidth trend is a signature of SARP and is indicative of adiabatic transfer of a large portion of the ground state population.

Figure 2 shows the (2 + 1) REMPI from HD ($v = 4$) as a function of Stokes fluence while the Stokes frequency and

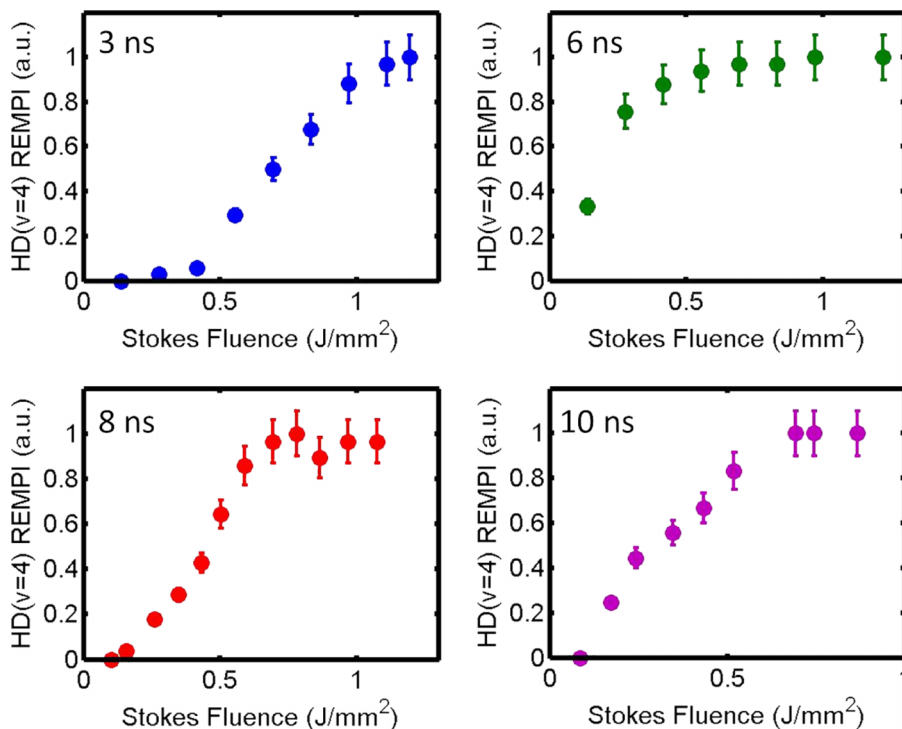


FIG. 2. Experimental (2+1) REMPI signal from SARP excited $X^1\Sigma_g^+$ HD ($v=4, J=0$) level as a function of Stokes fluence for the pump to Stokes delay of 3 ns, 6 ns, 8 ns, and 10 ns. The Stokes frequency is held constant at the peak value of the frequency detuning corresponding to the plots in Fig. 1 for each of the pump to Stokes delays. Pump fluence is approximately 12 J/mm^2 .

pump fluence are held constant. The Stokes frequency is fixed at the value corresponding to the peak obtained in Fig. 1 for each of the respective delays, and the pump fluence is held at approximately 12 J/mm^2 . Figure 2 shows that the saturation of $v = 4$ excitation against Stokes fluence is stronger for the pump to Stokes delays of 6 and 8 ns. This behavior might also seem to be counter-intuitive; it shows that in spite of a stronger overlap between the pump and the Stokes laser pulses, SARP saturates less readily for the shorter delay of 3 ns than at delays of 6 and 8 ns. The nature of this saturation is a hallmark of a successful adiabatic passage and should not be confused with the power saturation commonly observed in a high-pressure gas cell. In the absence of collisions in the molecular beam, the commonly observed power saturation is absent and the optical interaction is completely coherent in nature.

The nature of the frequency bandwidth and power saturation for the optimum 6-8 ns delay can be intuitively understood in the following way. SARP is based on the adiabatic following condition: $d\Delta/dt < 2\pi\Omega^2$. As has been previously described, in order to prevent the coherent return of population, the pump and probe pulses must be separated in time.¹³ Because the sweep rate ($d\Delta/dt$) is almost entirely determined by the intensity profile of the pump pulse and the two-photon Rabi frequency Ω is determined by the product of the pump and Stokes electric fields, there is an optimum delay for which the adiabatic condition is most easily satisfied. At this delay there simultaneously exist both a moderate sweep rate and a large Rabi frequency over a wide range of initial values of the detuning. Saturation is observed as long as the two-photon Rabi frequency exceeds the threshold value defined by $\Omega^2 \leq \frac{1}{2\pi}(d\Delta/dt)$, which is attained at a lower Stokes fluence with intermediate delays due to the lower sweeping rate. This intuitive explanation is supported by detailed theoretical calculations presented in the section titled Theory.

THEORY

In order to understand the seemingly anomalous spectral broadening and saturation characteristics present in the experimental data presented above, we have carried out a detailed theoretical simulation of the SARP process. This was done by solving density matrix equations for stimulated Raman pumping as described in our earlier work.² A 9.5 ns FWHM Gaussian pump pulse at 355 nm and a 5 ns FWHM Gaussian Stokes pulse at 680 nm are used for the calculation. As mentioned earlier, the Raman adiabatic process is controlled by two key dynamic parameters: (1) Stark tuning rate and (2) the Rabi frequency. These two parameters were varied in our theoretical simulation in order to best match our experimentally observed spectra.

Figure 3 displays the results of the theoretical simulation for SARP excitation from HD ($v = 0, J = 0$) to HD ($v = 4, J = 0$) as a function of Stokes detuning and Stokes fluence for a fixed pump fluence of 12 J/mm^2 for four different pump to Stokes delays of 3, 6, 8, and 10 ns. Because of the uncertainty in various experimental parameters such as optical fluence,

laser spot-size, and pulse shapes, any attempt to exactly fit the experimental data with theory will be extremely challenging if not impossible. Instead, we have made the calculations using the most reasonable laser beam parameters and, as previously mentioned, tried different values for the Raman polarizability and Stark tuning rate in order to closely match the characteristics of our experimental observations. A relative value of the Raman polarizability $r_{04}/r_{01} \approx 1/5$ and a Stark detuning rate of 75-85 MHz/(GW/cm²) best describe the experimentally observed spectrum and saturation curves in Figs. 1 and 2.

As can be seen in Fig. 3, good agreement between theory and experiment is achieved using these values for the parameters. The theory shows very clearly the increase in bandwidth at increasing delays, as well as the presence of a long flat region in the center of both the 6 and 8 ns delay frequency spectra. Our theoretical spectra are unable to exactly match our experiments, however. Noticeably absent from the theoretical spectra are the long tails in the experimental frequency spectra at 6, 8, and 10 ns. This discrepancy arises from the fact that our theoretical spectra are calculated using a single value for the pump fluence. However, as we will show later, increasing the pump fluence produces significantly wider frequency spectra. As previously noted, we have intentionally defocused the pump beam from the molecular beam in order to avoid off-resonant ionization of the HD. This defocusing will produce a variation in pump beam intensity across the molecular beam. The tail in the frequency spectrum is produced by the fact that our detection averages over the entire molecular beam, collecting molecules from regions with a variety of different pump intensities.

Good agreement is also achieved between the theoretical and experimental Stokes power spectra. We again see theory predicting the saturation of the transition, as well as the decrease in Stokes fluence required to achieve saturation at increased delays. It is worth noting that theory does not exactly match the value of the fluence at which saturation occurs for each delay, but this is again to be expected. We have been unable to precisely measure the spot size of the focused Stokes beam, so we instead use an estimate based on an indirect measurement to calculate the Stokes fluence. Additionally, day-to-day variations in beam shape and alignment produce different effective Stokes spot sizes. As such, the exact experimental values of the Stokes fluence are not known, but, importantly, the experimental spectra show a good qualitative match to the trend present in the theoretically predicted spectra.

The spectra displayed in Fig. 3 show the closest qualitative match we were able to find by varying the parameters discussed above. However, throughout our search of the parameter space, all of the theoretical spectra which were able to give anything close to a qualitative match to our experiments also showed a large transfer (80%-100%) of the HD population within the excitation volume. That is to say, as we go on to show in more detail below, our theory predicts that only by transferring significant percentages of the population, are we able to achieve the spectral shapes shown here.

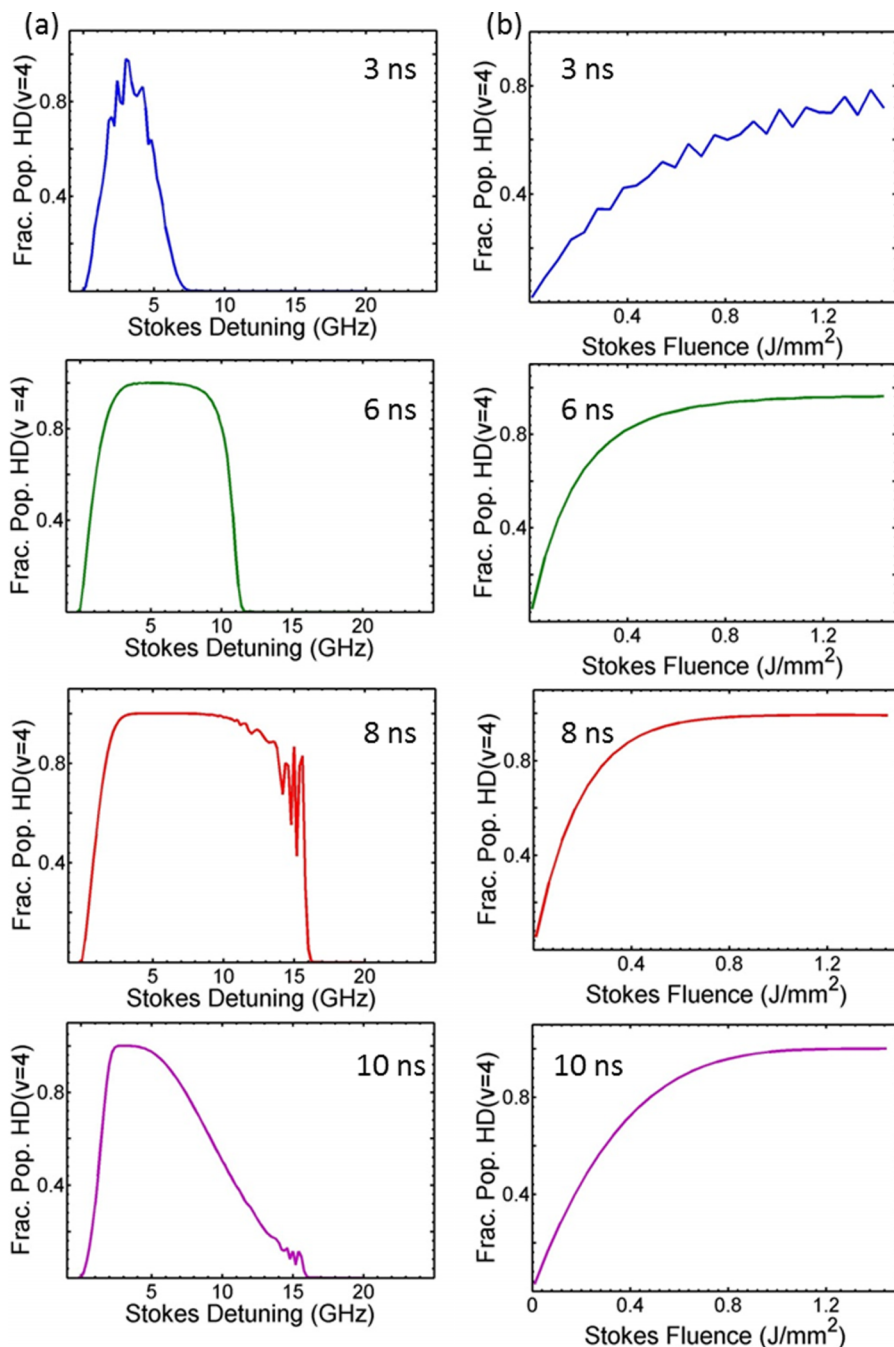


FIG. 3. Theoretical simulations of SARP frequency and power spectra using a value of $r_{04}/r_{01} = 1/5$ for the Raman polarizability and a Stark tuning rate of $80 \text{ MHz}/(\text{GW}/\text{cm}^2)$. A Gaussian pump pulse of 9.5 ns and a Gaussian Stokes pulse of 5 ns are used for the simulation. The pump fluence is held constant at $12 \text{ J}/\text{mm}^2$. (a) Fractional population transfer to the $v = 4$ level as a function of Stokes detuning for a fixed Stokes fluence of $1.3 \text{ J}/\text{mm}^2$ for various delays. (b) Fractional population transfer as a function of Stokes fluence for various delays. The Stokes frequency is held constant at the peak of the frequency detuning spectra shown in (a) for each of the pump to Stokes delays.

HOW LARGE IS THE RAMAN POLARIZABILITY?

The Raman polarizability for $v = 0$ to $v = 4$ transition has never been measured. In the past, both theory^{10,11} and experiment⁹ on Raman overtone transitions suggested that the Raman polarizability decreases by an order of magnitude with each increase in vibrational quantum number, i.e., $r_{02}/r_{01} \approx 1/10$ and $r_{03}/r_{01} \approx 1/100$. This is in sharp contrast to the value $r_{04}/r_{01} \approx 1/5$ which we have extracted by comparing our experimental data with theoretical predictions.

To further check the validity of the large Raman polarizability, we calculate the SARP spectrum and saturation curve using $r_{04}/r_{01} = 1/100$ for the pump to Stokes delays of 3-10 ns. Figure 4 displays the results of this theoretical simulation using the small polarizability. The frequency

spectra in Fig. 4(a) are calculated using a pump fluence of $12 \text{ J}/\text{mm}^2$ and a Stokes fluence of $1.3 \text{ J}/\text{mm}^2$ as in Fig. 3. These spectra look entirely different from the experimentally observed spectra displayed in Fig. 1. We have also calculated the excitation as a function of Stokes fluence for the fixed pump fluence ($12 \text{ J}/\text{mm}^2$) and a fixed Stokes frequency for each of the four delays. These results, displayed in Fig. 4(b), show excitation which is far from saturation, in direct contradiction with our experimental data. The oscillation in Fig. 4(b) for the pump to Stokes delay of 3 ns results from significant Rabi oscillations present in a situation where the adiabatic following condition is not fulfilled due to weaker Raman coupling. The contrast between the theoretical results of Fig. 4 and our experimental data (Figs. 1 and 2) clearly indicates that the relative Raman polarizability is significant for the

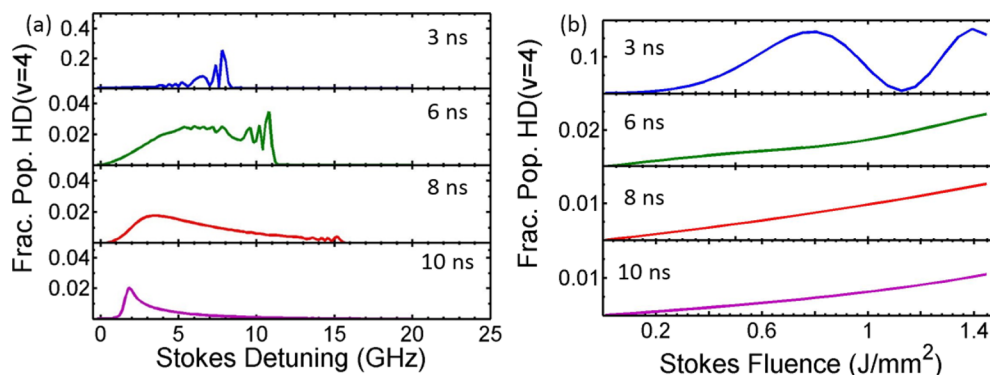


FIG. 4. Theoretical simulations of SARP frequency and power spectra using a value of $r_{04}/r_{01} = 1/100$ for the Raman polarizability. A Gaussian pump pulse of 9.5 ns and a Gaussian Stokes pulse of 5 ns are used for the simulation. The pump fluence and the Stark tuning rate are the same as in Fig. 3. (a) Fractional population transfer to the $v = 4$ level as a function of Stokes detuning for a fixed Stokes fluence of 1.3 J/mm^2 for various delays. (b) Fractional population transfer as a function of Stokes fluence for various delays. The Stokes frequency is held constant at the peak of the frequency detuning spectra shown in (a) for each of the pump to Stokes delays.

$v = 0$ to $v = 4$ transition. It is worth noting that the ratio of the Raman polarizabilities, $r_{04}/r_{01} \approx 1/5$, that best matches our experimental data, compares well with a recent theoretical value predicted by Chelkowski and Bandrauk.⁸ Thus, the Raman overtones do not necessarily decrease markedly in intensity, unlike infrared overtones. As such, the central idea presented in this paper is relatively general, in that there are very likely to be other molecules which have favorable vibrational wavefunction overlap, allowing efficient pumping of overtone Raman lines using SARP.

By fitting coherent anti-Stokes Raman data taken by Lucht and Farrow,¹⁴ we obtained an approximate value for r_{01} . This value, combined with our experiment, indicates an approximate value of the Raman polarizability for the $v = 0$ to $v = 4$ transition $\alpha_{00,40} \cong 0.6 \times 10^{-41} \text{ C m}^2 \text{ V}^{-1}$. We would like to point out that this value of the Raman polarizability is a

function of the pump frequency; however, for molecules like H_2 with a large energy gap between the ground and excited states, the dispersion of the polarizability is not strong.

DISCUSSION

To test further the validity of the Raman polarizability and confirm our successful adiabatic population transfer to the target $v = 4$ level, we repeated our measurements of the frequency and power spectra at a higher pump fluence of $\sim 23 \text{ J/mm}^2$ for the optimal pump to Stokes delays of 6 and 8 ns as shown in Fig. 5. These data show a slightly broader spectrum and a slightly slower rate of saturation compared to the data presented in Figs. 1 and 2. We also performed a theoretical simulation using a pump fluence of 23 J/mm^2 for the 6 and 8 ns delays to match the experiment described in

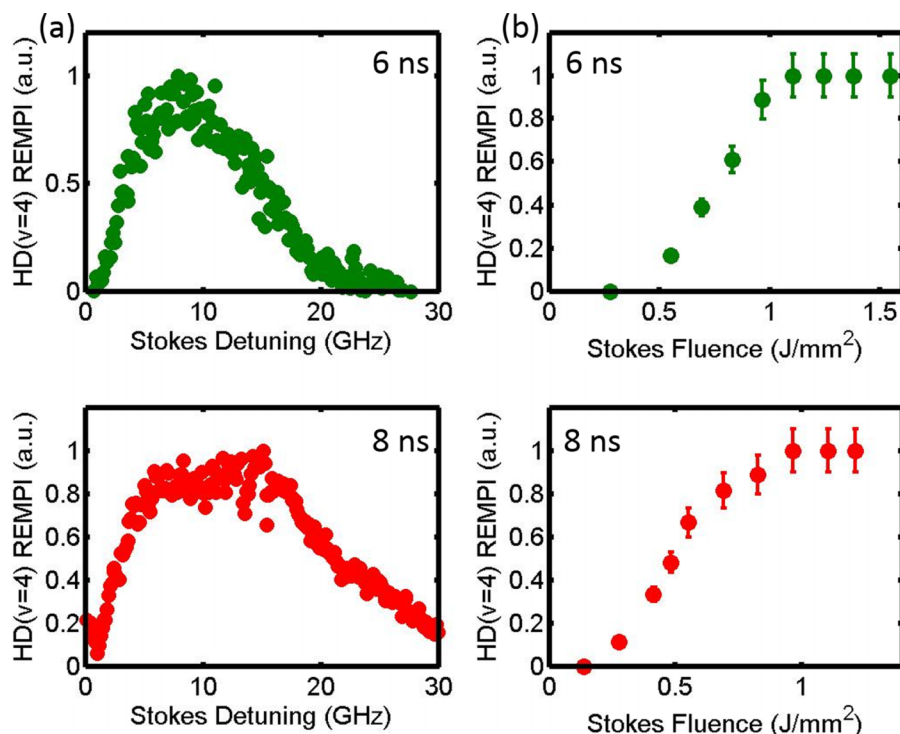


FIG. 5. Experimental frequency and power spectra for SARP excitation of HD ($v = 4, J = 0$) for the pump to Stokes delays of 6 and 8 ns for an approximate pump fluence of 23 J/mm^2 . (a) (2+1) REMPI signal from SARP excited $X \ ^1\Sigma_g^+$ HD ($v = 4, J = 0$) as a function of Stokes detuning for a fixed Stokes fluence of $\sim 1.3 \text{ J/mm}^2$ for the pump to Stokes delays of 6 and 8 ns. (b) (2+1) REMPI signal from $X \ ^1\Sigma_g^+$ HD ($v = 4, J = 0$) level as a function of Stokes fluence for the various delays. The Stokes frequency is held at the peak of the corresponding frequency detuning spectrum of (a).

Fig. 5. The calculated spectrum and power saturation plots qualitatively describe the experimental observations. Both theory and experiment show that the spectrum is wider for the pump to Stokes delay of 8 ns. The calculated saturation spectra correctly predict the onset of saturation near the Stokes fluence of 1 J/mm^2 . These measurements provide confirmation that higher pump powers do indeed produce wider frequency spectra which helps explain the experimentally observed frequency tail discussed above. The repeated agreement between experiment and theory for different pump and Stokes fluences not only allows an estimation of the hitherto unknown value for the Raman polarizability but also shows that using SARP we have achieved a near complete population transfer from the initial HD ($v = 0, J = 0$) to the final HD ($v = 4, J = 0$) level.

Using an estimated excitation volume of $2 \times 10^{-5} \text{ cm}^3$, a density of 10^{16} HD ($v = 0, J = 0$) molecules per cm^3 in the molecular beam, and assuming conservatively that only 10% of the molecules in that excitation volume are being pumped, we estimate a total of more than 10^{10} excited HD ($v = 4, J = 0$) molecules per laser pulse. Theory^{15–17} predicts a several order of magnitude enhancement of the collision cross sections going from the $v = 0$ to the vibrationally excited $v = 4$ state for molecular hydrogen colliding with different atoms and molecules. Based on this we believe that 10^{10} molecules will be sufficient for studying various scattering experiments with a significant signal-to-noise ratio.

In conclusion, we have reached an important milestone by preparing a single highly vibrationally excited ($v = 4$) level of a molecule using this adiabatic Raman method with commercially available nanosecond pump and Stokes laser pulses. Moreover, SARP is straightforward and can be applied to many other polar and nonpolar molecules, although Raman selection rules prevent the preparation of an arbitrary vibrational level of a polyatomic molecule.

The SARP process offers the experimentalist the ability to study fundamental collisions processes with a type of quantum state selection not easily realized by other means.

ACKNOWLEDGMENTS

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