THE JOURNAL OF PHYSICAL CHEMISTRY Letters

Letter

pubs.acs.org/JPCL

Highly Efficient Pumping of Vibrationally Excited HD Molecules via Stark-Induced Adiabatic Raman Passage

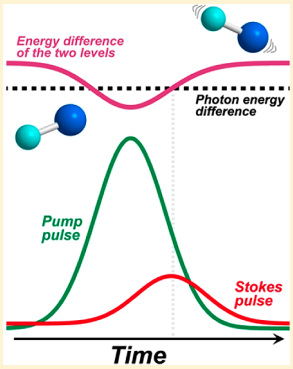
Tao Wang,[†] Tiangang Yang,[†,‡] Chunlei Xiao,*[,†] Dongxu Dai,[†] and Xueming Yang*[,†]

[†]State key Laboratory of Molecular Reaction Dynamics, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road Dalian 116023, China

[‡]School of Physics and Optoelectric Engineering, Dalian University of Technology, Dalian, Liaoning 116023, China

Supporting Information

ABSTRACT: A primary prerequisite to study reactivity of vibrationally excited species is to efficiently prepare reacting species in a well-defined vibrational level. Efficient pumping of IR active vibrational modes in a molecule can be achieved by direct IR absorption. For vibrational modes that are only Raman active, however, efficient preparation of vibrationally excited states in those modes is not easily attainable. In this work, we have shown that highly efficient preparation of the HD(v = 1) state using the Stark-induced adiabatic Raman passage (SARP) scheme is feasible. As high as 91% population transfer from v = 0 to 1 of HD has been demonstrated in our experiment. This method provides new opportunities for future experimental studies on the dynamics of vibrational state molecules, especially H_2, in both gas-phase and beam-surface reactions.



SECTION: Kinetics and Dynamics

Effects of reagent vibrational excitation on chemical reactivity have received great attention[1−6] in the past few decades because they are intimately related to bond- and mode-selective chemistry. Preparation of vibrationally excited species efficiently is a prerequisite for experimental studies of reaction dynamics of excited molecules. For vibrational states of IR active modes, efficient pumping can be achieved by direct IR excitation using strong narrow-bandwidth IR lasers. This has been widely applied in the study of chemical reactivity of vibrationally excited species in the past decades. For vibrational excited states of only Raman active modes, such as H_2 vibration and C−H symmetric stretch vibration of CH_4, efficient excitation is difficult. Stimulated Raman pumping (SRP) is widely used to prepare vibrational excitation of nonpolar molecules in the molecular beam scattering experiment. For example, Zare and coworkers prepared vibrationally excited H_2, HD, and CH_4 using SRP for reactive scattering experiments with D and Cl atoms in the "photoloc" approach.[7−9] Beck and coworkers used SRP to perform quantum-state resolved gas-surface reactivity measurements for CH_4 prepared in its symmetric C−H stretch vibration on a Ni(100) single crystal surface.[10] However, the excitation efficiency using SRP is usually not very high.

In the SRP process, two coherent laser fields interact simultaneously with a molecule via its nonlinear polarizability. When the frequency difference between the incident laser fields equals the frequency of a Raman active vibrational mode in a molecule, energy is transferred from the pump laser field to the Stokes field, leaving the molecule in a vibrationally excited state.[11] For vibrationally excited molecules in a molecular beam, however, SRP suffers from two difficulties that prevent high excitation efficiency. First, narrow-bandwidth and high-power laser pulses are necessary to enhance the SRP efficiency, but the dynamic Stark shift induced by the pump and Stokes laser pulses will throw the system off resonance.[12] Second, temporal overlap of the pump and Stokes pulse will cause coherent population return (CPR), which will bring the excited population back to the ground state,[13,14] thus reducing the SRP efficiency.

To overcome these limitations, Zare and Mukherjee proposed the scheme of Stark-induced adiabatic passage (SARP),[13] an important extension of adiabatic passage techniques to excite Raman active vibrations using a virtual intermediate state. Adiabatic passage techniques,[14] including stimulated Raman adiabatic passage (STIRAP),[15] vibrational ladder climbing,[16] and Stark-chirped rapid adiabatic passage (SCRAP),[17,18] are a series of coherent highly efficient population transfer methods that use real intermediate states, which are not accessible for many important molecules using strong lasers in the visible and ultraviolet regions. The proposed SARP scheme, however, does not need any such real intermediate state.

Numerical simulations by Zare and Mukherjee suggested that near complete population transfer of H_2 from the vibrationally

Received: December 18, 2012
Accepted: January 9, 2013
Published: January 9, 2013

ground state to the excited state is possible. In this scheme, the frequency difference of the pump and Stokes laser is tuned closed to, but not exactly to, the Raman resonance frequency. The pump and Stokes pulses are temporally displaced with unequal intensities. The stronger pulse induces the dynamical Stark shift and sweeps the molecular energy level through Raman resonance frequency. The zero-crossing or adiabatic crossing happens only once during the course of Raman interaction, so the CPR can be prevented.[13] This is clearly a very attractive technique. Recently, we have developed a laser system that is suitable to test this SARP scheme. Here we report the experimental demonstration of highly efficient population transfer of the HD molecule from $v = 0$ to 1 using the SARP scheme.

The laser system used in the SARP pumping scheme in this experiment consists of two frequency-stabilized, injection-seeded Nd:YAG lasers and a home-built narrow-bandwidth optical parameter oscillator/amplifier system (OPO/OPA). A transform-limited laser pulse from doubling of an injection-seeded Nd:YAG laser (Continuum) acted as the Raman pump pulse, with a pulse duration of ~8 ns and pulse energy of 270 mJ. The Stokes laser pulse was generated in an OPO/OPA system developed based on an OPO system by Wodtke and coworkers.[19] Pumped by 180 mJ of the second harmonics of an injection-seeded Nd:YAG laser (Continuum, PL8000 DLS), this home-built system can generate Fourier-transform-limited pulses of ~55 mJ with a duration of ~6 ns at 660 nm. The 660 nm Stokes laser beam and the 532 nm pump laser beam were then combined collinearly by a dichroic mirror and then focused into a HD molecular beam, which was generated by expanding a pure HD sample through a pulsed nozzle (Even-Lavie valve) with a backing pressure of 100 psi. The two laser beams were focused to a diameter size of ~0.25 mm in the HD beam. The laser frequencies were monitored by a high-resolution wavemeter (HighFinesse, WS7). A computer control program was used to stabilize the frequency difference of the pump and Stokes lasers to within 50 MHz. This high stability is crucial to achieving high pumping efficiency. Both the pump and Stokes lasers were vertically polarized. These lasers were used to pump the HD molecules from $(v = 0, j = 0)$ to $(v = 1, j = 0)$ via the SARP scheme. The 532 nm pump laser pulse also acted as the Stark shifting pulse. For REMPI detection of the HD molecules, a third Nd:YAG pumped tunable dye laser beam, operating between 603 and 630 nm, was frequency-tripled to 201−210 nm using a DKDP crystal and a β-BBO crystal. About 0.3 mJ of laser pulse in the region of 201−210 nm was generated and used to detect the HD molecules in $(v = 0, j = 0)$ and $(v = 1, j = 0)$ levels using a (2 + 1) REMPI scheme via the $E/F\ ^1\Sigma_g^+$ electronic state. The probe laser was reduced to a spot size of ~0.1 mm diameter and spatially overlapped with the excitation region. The relevant energy levels of the HD molecule and the timing sequence for the pump and Stokes lasers and the HD REMPI detecting laser are illustrated in Figure.1. A fast photodiode and an oscilloscope (Tektronix TDS5054) were used to determine the exact timing of the pump, Stokes, and probe pulses. The timing of the three lasers and the data acquisition system was controlled by a digital delay generator system (SRS DG535). The time delay between the pump and Stokes lasers can be varied to map out the pumping efficiency time profile. The REMPI laser was set to be 40 ns after the 532 nm pump laser pulse (see Figure 1). We have changed this time delay considerably, no change in the REMPI signal has been observed.

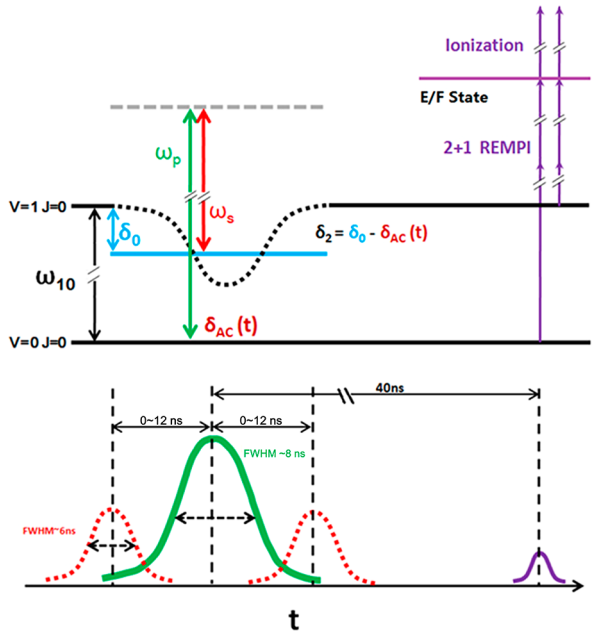


Figure 1. Schematic diagram for SARP pumping of HD and REMPI detection via the $E/F\ ^1\Sigma_g^+$ electronic state. In the lower frame, the temporal profile of the pump, Stokes, and detection laser pulses are show in green, red, and purple, respectively. The relevant energy levels are shown in the upper frame. The Stark shift of the $(v = 1, J = 0)$ induced by the pump pulse is exaggerated for clarity (black dashed curve). δ_0 is zero-field detuning. δ_{AC} is dynamic Stark shift induced by SARP lasers. δ_2 is Raman detuning. ω_p and ω_s are angular frequency of the pump and the Stokes lasers, respectively.

Using the above experimental scheme, we have measured the HD REMPI lines from HD$(v = 0, j = 0)$ and HD$(v = 1, j = 0)$ with the Stokes laser on and off. The REMPI transitions from HD$(v = 0, j = 0)$ and HD$(v = 1, j = 0)$ are shown in Figures 2 and 3, respectively. The REMPI lines were measured under the optimal conditions for the highest pumping efficiency achievable. Under these conditions, the HD molecules were excited from $(v = 0, j = 0)$ to $(v = 1, j = 0)$ at the fixed energy

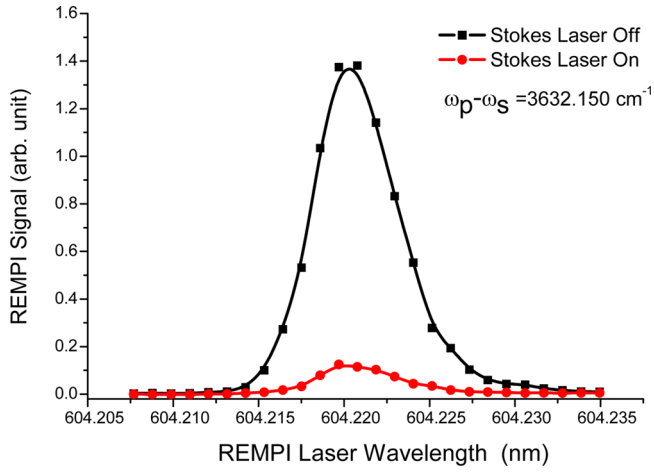


Figure 2. REMPI transition line from HD$(v = 0, J = 0)$ level, with the Stokes laser on and off, respectively. The 91.3% depletion of the peak area indicates that 91.3% population of the HD$(v = 0, J = 0)$ is transferred to the upper state via the SARP scheme under the best experimental conditions.

dx.doi.org/10.1021/jz302103u | J. Phys. Chem. Lett. 2013, 4, 368−371

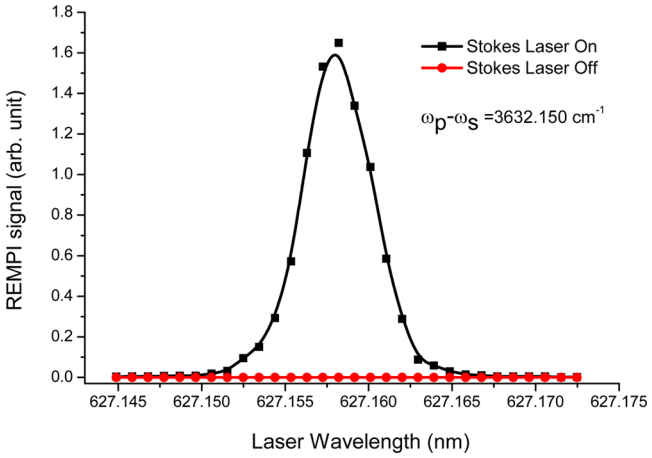


Figure 3. REMPI transition line from HD(v = 1,J = 0), with the Stokes laser on and off, respectively.

difference of the pump and Stokes laser pulses, $\Delta\omega$ = 3632.150 cm^{-1}, with λ_P = 532.21549 nm and λ_S = 659.75176 nm. The optimal time delay between the pump and Stokes laser pulses, for the highest HD pumping efficiency, was found to be around 2 ns between the 532 nm pump and 659 nm Stokes laser pulses, with the Stokes laser behind the pump laser. From Figure 2, it is clear that the HD(v = 0, j = 0) population, detected via REMPI, is depleted dramatically when the Stokes laser is on, whereas from Figure 3, the HD(v = 1,j = 1) population is observable only when the Stokes laser is on. This suggests that large population is transferred from the HD(v = 0, j = 0) level to HD(v = 1, j = 0) using this pumping scheme. Because the REMPI signals from the two levels cannot be compared quantitatively, we used the population depletion of the HD(v = 0, j = 0) level to measure the pumping efficiency. Under the optimal condition, a 91.3% depletion of HD(v = 0, j = 0) population has been observed. This 91.3% depletion represents the best absolute pumping efficiency from HD(v = 0, j = 0) to HD(v = 1, j = 0) achievable under the current experimental conditions. This result clearly demonstrates that very high population transfer can be achieved using the scheme described above.

It should be noted that the pump and Stokes laser pulses were not fully temporally overlapped for optimal pumping efficiency. This is the main difference between SRP and SARP schemes and suggests that the pumping process used here to pump HD from v = 0 to 1 is indeed a SARP process, in which the 532 nm laser serves as the main Stark shifting laser. Another big difference is that no more than 50% of the ground state can be pumped to the vibrationally excited state in the SRP scheme. In the current experiment, however, we have achieved as high as 91.3% pumping efficiency of HD from v = 0 to 1. This demonstrates that the pumping process in this experiment is a SARP process, which is proposed by Zare and Mukherjee.[13]

To reveal the relation between the time delay and the excitation efficiency, we fixed the energy difference of pump and Stokes photons at $\Delta\omega$ = 3632.150 cm^{-1} and then measured the excitation efficiency at different time delay at 1 ns intervals. There were two ways to measure the excitation efficiency: (a) measuring the difference of areas of the (v = 0, J = 0) REMPI spectral peaks without and with Stokes laser, led to the absolute excitation efficiency and (b) measuring the area of the HD(v = 1, J = 0) REMPI spectral transition will give us the relative excitation efficiency, as we did in measuring these data in Figures 2 and 3. Figure 4 shows the dependence of the measured pumping efficiencies on the time-delay between the

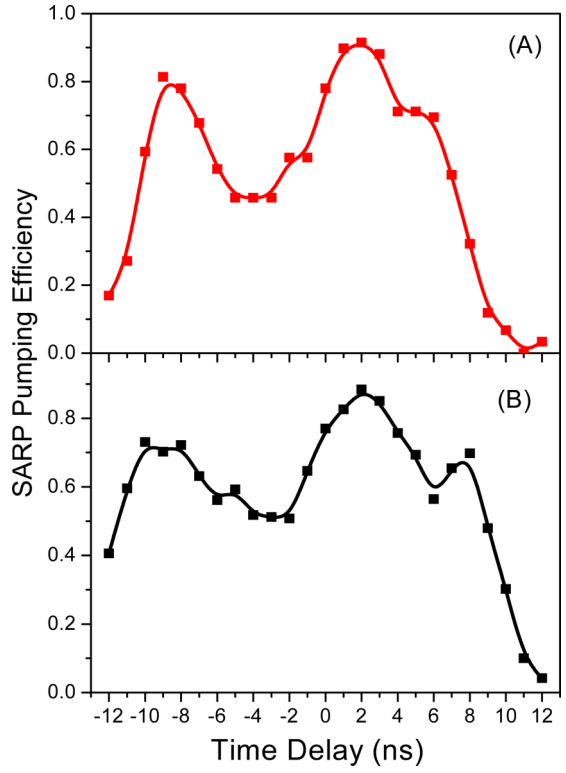


Figure 4. Dependence of the SARP excitation efficiency on the time delay between the pump and Stokes laser pulses. (A) HD(v = 0,J = 0) excitation efficiency. (B) Total HD(v = 1,J = 0) population detected via (2 + 1) REMPI, scaled to the absolute excitation efficiency in panel A at 2 ns time delay.

pump and Stokes laser pulses. Figure 4A shows the absolute pumping efficiencies obtained from measuring the HD(v = 0, j = 0) population change; while Figure 4B shows the relative pumping efficiencies obtained from measuring the relative HD(v = 1, j = 0) population. The relative efficiencies in Figure 4B are scaled assuming the relative efficiency is same to Figure 4A at time delay of 2 ns. The time-delay dependence profiles for the two measurements are very similar to each other, suggesting that we are probing the exactly same SARP process via different REMPI transitions. It is quite clear from Figure 4 that the optimal pumping efficiency in the SARP scheme is not at time delay zero, in agreement with the theoretical prediction. However, we found that the minimum pumping efficiency is also not at time-delay zero. The minimum pumping efficiency in our experiment is shown at time delay of −4 ns. As a result, the time-delay dependence curve of the pumping efficiency is clearly not symmetric with respect to time-delay zero. Another maximum pumping efficiency (up to 80%) is also detected around −8 ns, which means that the Stokes laser pulse is ahead of the 532 nm pump pulse with only partial overlap between the two pulses, which is characteristic of a SARP process. This is also similar to that of a STIRAP process.[15] The temporal profiles of Stokes pulse feature a fast rising edge and a slow trailing edge (Figure S2 in the Supporting Information). The deviation of the temporal profile of Stokes pulse from a perfect Gaussian shape is considered to be the main reason for the

dx.doi.org/10.1021/jz302103u | J. Phys. Chem. Lett. 2013, 4, 368−371

asymmetric shape curve (Figure 4) with respect to zero time-delay.

In summary, we have successfully demonstrated that highly efficient population transfer from the HD vibrational ground state to the HD $v = 1$ excited state is feasible using the SARP scheme. As high as 91.3% pumping efficiency has been achieved in pumping HD from $v = 0$ to 1. It should be noted here that this novel SARP is not limited to molecular hydrogen. Rather, it should be a universal excitation scheme for Raman-active mode vibrations, including vibration of homonuclear diatomics and totally symmetric vibrations of polyatomic molecules. The enhanced efficiency using the SARP scheme opens the door for interesting reaction dynamics studies in the gas phase and at surfaces for vibrationally excited species in those modes that are only Raman-active.

■ ASSOCIATED CONTENT

Supporting Information

Schematic diagram for the laser system and the experimental setup for the SARP experiment. The temporal profiles of the pump and Stokes pulses. The REMPI signal of HD($v = 1$,$j = 0$) as a function of detuning and time-delay. The jitter of the pump and Stokes pulses. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: chunleixiao@dicp.ac.cn (C.X.); xmyang@dicp.ac.cn (X.Y.).

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We would like to thank Dr. Cunshun Huang for bringing our attention to this interesting topic. X.Y. also thanks Prof. Richard Zare for his inspiring lecture on SARP at the 2011 COMET meeting. This work was funded by the Chinese Academy of Sciences, the Ministry of Science and Technology, and the National Natural Science Foundation of China.

■ REFERENCES

(1) Polanyi, J. C. Some Concepts in Reaction Dynamics. *Science* **1987**, *236*, 680−690.

(2) Crim, F. F. Vibrational State Control of Bimolecular Reactions: Discovering and Directing the Chemistry. *Acc. Chem. Res.* **1999**, *32*, 877−884.

(3) Zare, R. N. Laser Control of Chemical Reactions. *Science* **1998**, *279*, 1875−1879.

(4) Crim, F. F. Chemical Dynamics of Vibrationally Excited Molecules: Controlling Reactions in Gases and on Surfaces. *Proc. Natl. Acad. Sci. U.S.A.* **2008**, *105*, 12654−12661.

(5) Wang, F. Y.; Liu, K. P. Enlarging the Reactive Cone of Acceptance by Exciting the C-H Bond in the $O(^3P) + CHD_3$ Reaction. *Chem. Sci.* **2010**, *1*, 126−133.

(6) Palma, J.; Echave, J.; Clary, D. C. The Effect of the Symmetric and Asymmetric Stretching Vibrations on the $CH_3D+O(^3P) \rightarrow CH_3+OD$ reaction. *Chem. Phys. Lett.* **2002**, *363*, 529−533.

(7) Kliner, D. A. V.; Adelman, D. E.; Zare, R. N. Comparison of Experimental and Theoretical Integral Cross-Sections for D $+H_2$(v=1,j=1) → HD(v′=1,j′)+H. *J. Chem. Phys.* **1991**, *95*, 1648−1662.

(8) Simpson, W. R.; Orr-Ewing, A. J.; Zare, R. N. State-to-State Differential Cross-Sections for the Reaction $Cl(^2P_{3/2})+CH_4(v_3=1,j=1) \rightarrow HCl(v'=1,j')+CH_3$. *Chem. Phys. Lett.* **1993**, *212*, 163−171.

(9) Kandel, S. A.; Alexander, A. J.; Kim, Z. H.; Zare, R. N.; Aoiz, F. J.; Banares, L.; Castillo, J. F.; Rabanos, V. S. Cl + HD (v=1; j=1,2) Reaction Dynamics: Comparison Between Theory and Experiment. *J. Chem. Phys.* **2000**, *112*, 670−685.

(10) Maroni, P.; Papageorgopoulos, D. C.; Sacchi, M.; Dang, T. T.; Beck, R. D.; Rizzo, T. R. State-resolved Gas-surface Reactivity of Methane in the Symmetric C-H Stretch Vibration on Ni(100). *Phys. Rev. Lett.* **2005**, *94*, 246104−246107.

(11) Maroni, P.; Papageorgopoulos, D.; Ruf, A.; Beck, R. D.; Rizzo, T. R. Efficient Stimulated Raman Pumping for Quantum State Resolved Surface Reactivity Measurements. *Rev. Sci. Instrum.* **2006**, *77*, 054103−054108.

(12) Mukherjee, N.; Zare, R. N. Can Stimulated Raman Pumping Cause Large Population Transfers in Isolated Molecules? *J. Chem. Phys.* **2011**, *135*, 184202−184208.

(13) Mukherjee, N.; Zare, R. N. Stark-Induced Adiabatic Raman Passage for Preparing Polarized Molecules. *J. Chem. Phys.* **2011**, *135*, 024201−024210.

(14) Vitanov, N. V.; Halfmann, T.; Shore, B. W.; Bergmann, K. Laser-Induced Population Transfer by Adiabatic Passage Techniques. *Annu. Rev. Phys. Chem.* **2001**, *52*, 763−809.

(15) Gaubatz, U.; Rudecki, P.; Schiemann, S.; Bergmann, K. Population Transfer between Molecular Vibrational Levels by Stimulated Raman Scattering with Partially Overlapping Laserfields. A New Concept and Experimental Results. *J. Chem. Phys.* **1990**, *92*, 5363−5376.

(16) Maas, D. J.; Duncan, D. I.; van der Meer, A. F. G.; vanderZande, W. J.; Noordam, L. D. Vibrational Ladder Climbing in NO by Ultrashort Infrared Laser Pulses. *Chem. Phys. Lett.* **1997**, *270*, 45−49.

(17) Rickes, T.; Yatsenko, L. P.; Steuerwald, S.; Halfmann, T.; Shore, B. W.; Vitanov, N. V.; Bergmann, K. Efficient Adiabatic Population Transfer by Two-Photon Excitation Assisted by a Laser-Induced Stark Shift. *J. Chem. Phys.* **2000**, *113*, 534−546.

(18) Oberst, M.; Munch, H.; Halfmann, T. Efficient Coherent Population Transfer among Three States in NO Molecules by Stark-Chirped Rapid Adiabatic Passage. *Phys. Rev. Lett.* **2007**, *99*, 173001−173004.

(19) Velarde, L.; Engelhart, D. P.; Matsiev, D.; LaRue, J.; Auerbach, D. J.; Wodtke, A. M. Generation of Tunable Narrow Bandwidth Nanosecond Pulses in the Deep Ultraviolet for Efficient Optical Pumping and High Resolution Spectroscopy. *Rev. Sci. Instrum.* **2010**, *81*, 063106−063115.