斯塔克诱导绝热通道过程选择性地制备振动激发单态和量子态叠加

引言

To perform a fully quantum mechanical study if inelastic and collisions in a laboratory setting need to prepare a large population of target molecules in a single vibrational (ν), rotational (J), and magetic (M) quantum state.

How Can a Large Ensemble of Molecular Targets be Prepared in a Selected Highly Vibrationally Excited Quantum State With Rotational (J, M) Quantum Number Precision?

To obasrve single colliision0-free ambience of a dilute molecular gas or in molecular beam.

Optival methods:

- Raman scattering
- Franck-Condon pumping
- emission pumping
- chirped pulse infrared ladder excitation

Raman adiabatic pumping

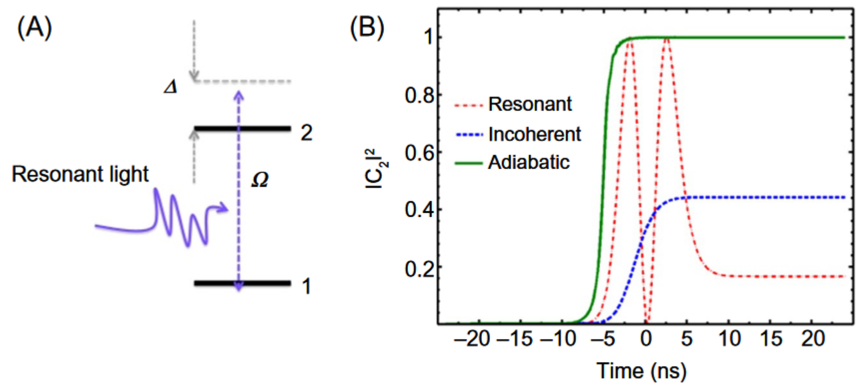


FIG. 1 (A) Optical excitation of a two-level system. Ω is the Rabi frequency for $|1\rangle \rightarrow |2\rangle$ transition, and Δ is the resonance detuning. (B) Comparison of an adiabatic passage process with Rabi oscillations and incoherent population transfer in a collisionally damped system. $|C_2|^2$ gives the fractional population in the excited state $|2\rangle$. We examine mathematically these three situations later in the text.

Fig. 1 describes three typical situations where the ground and excited states are optically coupled by single or multiphoton resonance interaction represented by the coupling strength Ω.

- Resonant: the familiar Rabi oscillations
- Incoherent: the presence of collisional damping
- Adiabatic: an adiabatic passage process

Rabi oscillations in a consistent manner need to precisely control the frequency and energy of the pulse

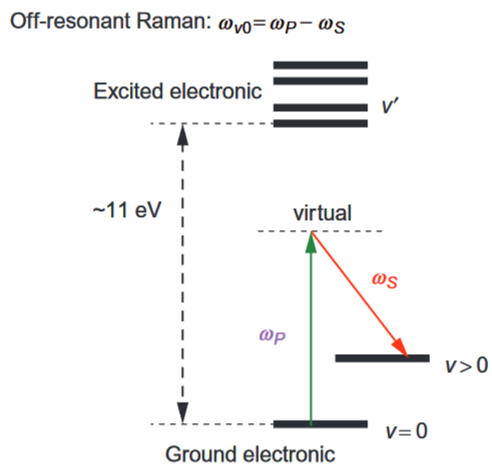


FIG. 2 Stimulated Raman pumping of the ground vibrational ($v = 0$) level to a higher vibrational level within the ground electronic $X^1\Sigma_g^+$ state of the H_2 molecule.

$$H_{int} = -\vec{\mu} \cdot \vec{E}(t)$$

$$|\Psi(t)\rangle = c_1(t)|1\rangle + c_2(t)|2\rangle + \sum_{k\neq 1,2} c_k(t)|k\rangle$$

$$i\hbar \frac{\mathrm{d}|\Psi(t)\rangle}{\mathrm{d}t} = (H_0 + H_{int})|\Psi(t)\rangle$$

$$\frac{\mathrm{d}c_1}{\mathrm{d}t} = -\frac{\vec{\mu}_{1k} \cdot \vec{E}}{\hbar} \exp\left[i\omega_{1k}t\right]$$

$$\frac{\mathrm{d}c_2}{\mathrm{d}t} = -\frac{\vec{\mu}_{2k} \cdot \vec{E}}{\hbar} \exp\left[i\omega_{2k}t\right]$$

$$\left(\frac{\mathrm{d}c_k}{\mathrm{d}t}\right)_{k\neq 1,2} = -\frac{\vec{\mu}_{k1} \cdot \vec{E}}{\hbar} \exp\left[i\omega_{k1t}t\right] c_1 - \frac{\vec{\mu}_{k2} \cdot \vec{E}}{\hbar} \exp\left[i\omega_{k2}t\right] c_2$$

$$\frac{\mathrm{d}}{\mathrm{d}t}\begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = -i\begin{bmatrix} \Delta_{11} & \Omega_{12} \\ \Omega_{21} & \Delta_{22} \end{bmatrix}\begin{pmatrix} c_1 \\ c_2 \end{pmatrix}$$

$$\Delta_{ii} = -\left[\alpha_i(\omega_P)|E_P|^2 + \alpha_i(\omega_S)|E_S|^2\right]/\hbar$$

$$\Omega_{12} = \frac{r_{12}}{\hbar} E_P E_S^* \exp\left[i\delta_{12} t\right]$$

$$r_{12} = \frac{1}{\hbar}\sum_{k\neq 1,2} \mu_{1k}\mu_{k2}\left[\frac{1}{\omega_{k1} - \omega_P} + \frac{1}{\omega_{k1} + \omega_S}\right]$$

Densty Matirx Equation

$$\rho = \begin{bmatrix} \rho_{11} & \rho_{12} \\ \rho_{21} & \rho_{22} \end{bmatrix}$$

$$\rho_{11} = |c_1|^2, \quad \rho_{22} = |c_2|^2, \quad \text{and} \quad \rho_{12} = c_1 c_2^*$$

$$\frac{\mathrm{d}\rho_{12}}{\mathrm{d}t} + i\Delta\rho_{12} = 2i\Omega_{12}w$$

$$\frac{\mathrm{d}w}{\mathrm{d}t} = 2\Im[\Omega_{12}^*\rho_{12}]$$

Stauration of Raman Pumping in a High-Pressure Gas Cell

$$\rho_{12} = \left(\frac{2\Omega_{12}}{\Delta - i\gamma} \right) w$$

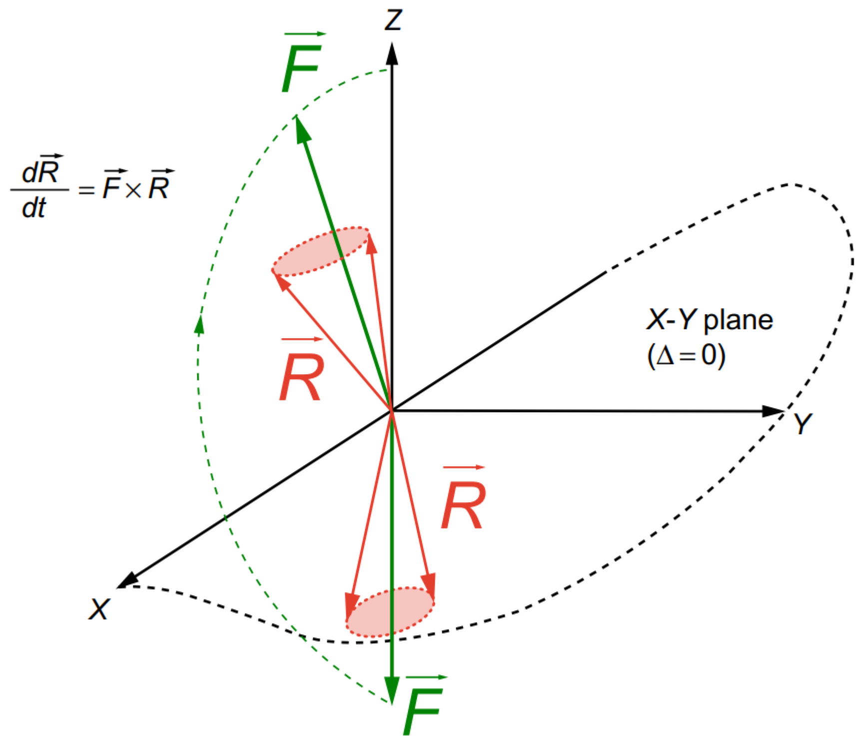
$$w(t) = w(0) \exp \left[-4 \int_0^t \left(\Omega_{12}^2 / \gamma \right) \mathrm{d}t \right]$$

$w(t = 0) = -1/2$ *in the absence of Raman pumping.*

Bloch Vecrot Model for Stark-Induced Adiabatic Passage

$$\frac{\mathrm{d}\vec{R}}{\mathrm{d}t} = \vec{F} \times \vec{R}$$

$\vec{R} = [\mathrm{Re}(\rho_{12}), \mathrm{Im}(\rho_{12}), w]$, $\vec{F} = [2\Omega_{12}, 0, -\Delta]$



Z
$\vec{F}$
$\frac{d\vec{R}}{dt} = \vec{F} \times \vec{R}$
$\vec{R}$
X-Y plane
$(\Delta = 0)$
Y
$\vec{R}$
X
$\vec{F}$

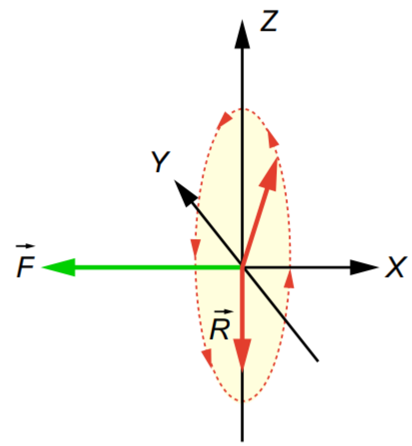
Bloch-Feynman vector model for the Stark-induced adiabatic passage process. The Bloch vector $\vec{R}$ *represents the molecular state, while the field vector* $\vec{F}$ *refers to the combined optical field of the pump and Stokes pulses that drive the Raman transition. In the pseudo space, the Z-component of the Bloch vector* $\vec{R}$ *refers to population inversion between the initial and final vibrational levels. Note that as the Raman detuning* Δ *changes due to the light-induced Stark shift, the* Z*-component of* $\vec{F}$ *passes through the X-Y plane of the pseudo space and reverses the sign. If* $\vec{R}$ *spins around* $\vec{F}$ *fast enough and* $\vec{F}$ *changes slowly enough,* $\vec{R}$ *will be able to follow* $\vec{F}$*, eventually also inverting along* Z*. Inversion of* R *along* Z *corresponds to inversion of population between the initial and final vibrational levels. This is adiabatic population inversion.*

$$\frac{\mathrm{d}|\vec{F}|}{\mathrm{d}t}\frac{1}{|\vec{F}|} < |\vec{F}| \tag{19}$$

$$\frac{\mathrm{d}\Delta}{\mathrm{d}t} < 2\pi\Omega_{12}^{2} \tag{20}$$

Rabi Oscillatins

$$
\begin{aligned}
\mathrm{Im}(\rho_{12}) &= -\frac{1}{2}\sin\Omega_{12}t \\
w(t) &= \frac{1}{2}\cos(\Omega_{12}t)
\end{aligned}
\tag{21}
$$

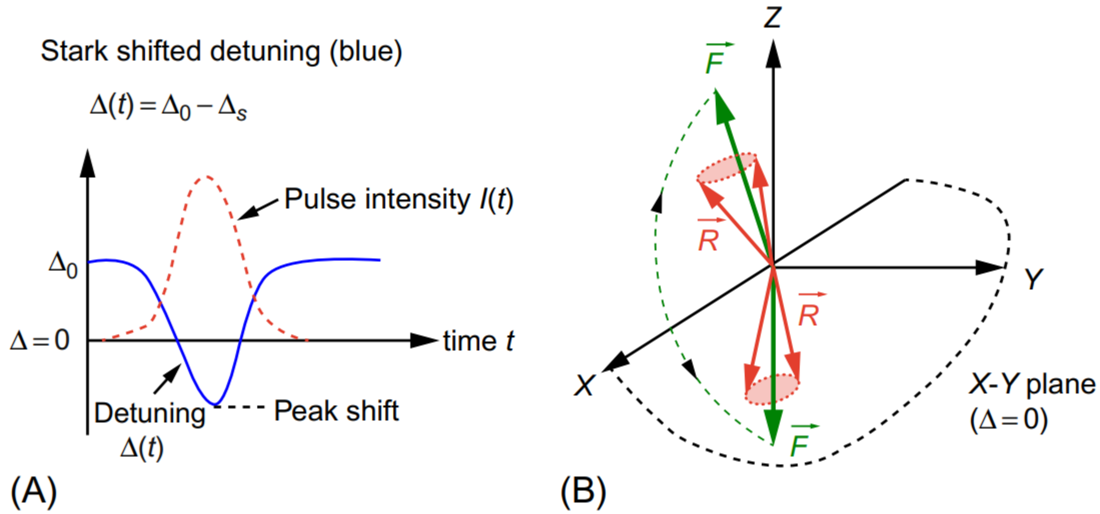


Rabi Oscillations of population and Tanman cierence between te inintial and traget vibratinal levles as described by the rotatino of the Bloch vector $\vec{R}$ *around a field vector* $\vec{F}$ *whose direciton remains constant(along the X-axis of the pseudo space). The rottation of Block vector* $\vec{R}$ *takes place in Y-Z plane of thhe pseudo space.*

Coherent Population Return is a Problem for Stark-Induced Population Transfer

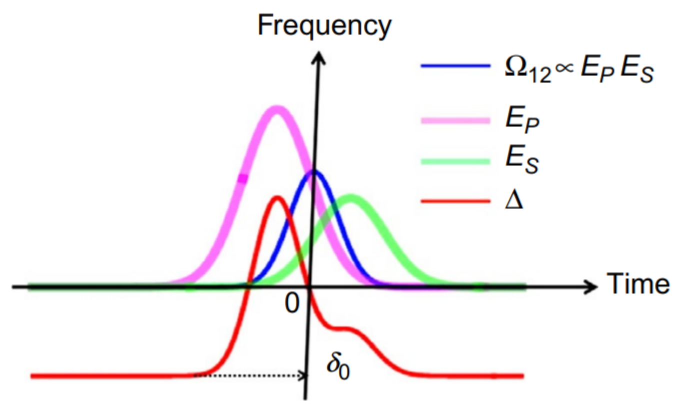
$$\Delta \approx \delta_0 - \Delta_{AC} \tag{22}$$

$$\Delta_{AC} = \frac{(\alpha_2 - \alpha_1)}{\hbar} \left[|E_P|^2 + |E_S|^2 \right] \tag{23}$$


Stark shifted detuning (blue)
$\Delta(t) = \Delta_0 - \Delta_s$
Pulse intensity $I(t)$
Δ_0
$\Delta = 0$
time t
Detuning
$\Delta(t)$
Peak shift
(A)
Z
$\vec{F}$
$\vec{R}$
$\vec{R}$
Y
X
$\vec{F}$
X-Y plane
($\Delta = 0$)
(B)

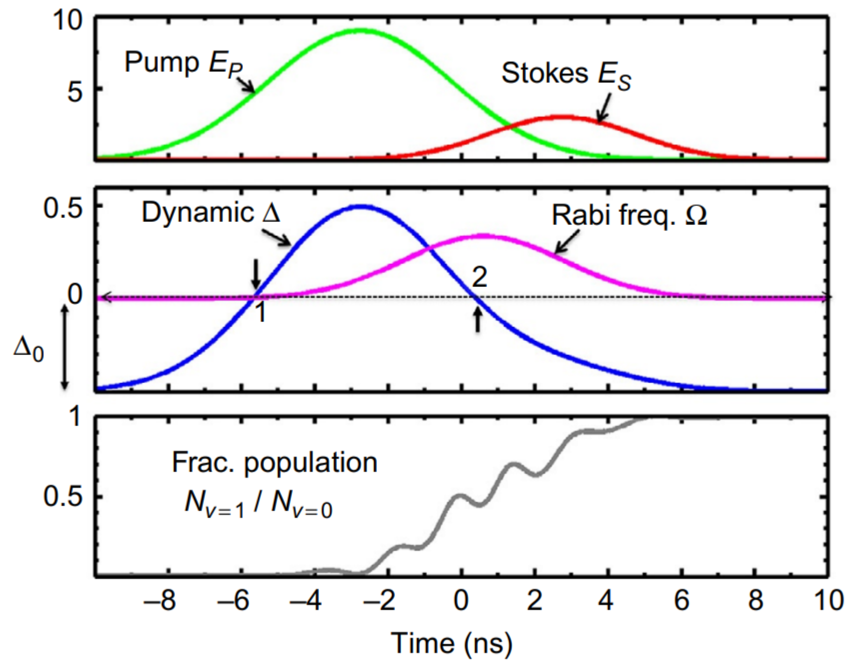
How Do We Accomplish Stark-Induced Adiabatic Passage Using Pulsed Excitation?

the threshold condition for SARP depends on two key parameters, the Raman polarizability (r_{0v}) and the difference of the optical polarizabilities ($\Delta\alpha_{00\to vj}$) of the initial ($v = 0, j = 0$) and the target (v, j) rovibrational levels.



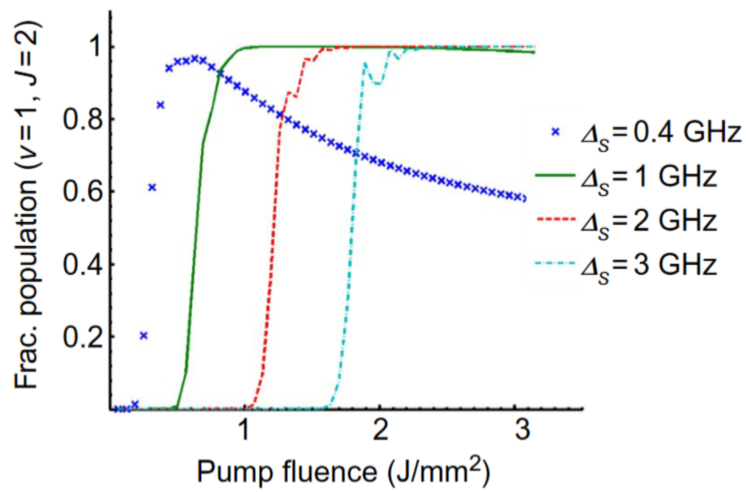
The dynamic detuning Δ *(red) and Rabi frequency* Ω *(blue) in the presence of a delayed sequence of a strong pump pulse (purple) partially overlapping with a weaker Stokes pulse (green). The Rabi frequency* Ω *is strong only at one of the two zero-crossings of the detuning* Δ*, thus ensuring unidirectional flow of population from the initial to the target level.*

Theoretical simulation of sarp for H_2 $(v = 0 \rightarrow v = 1)$ translations

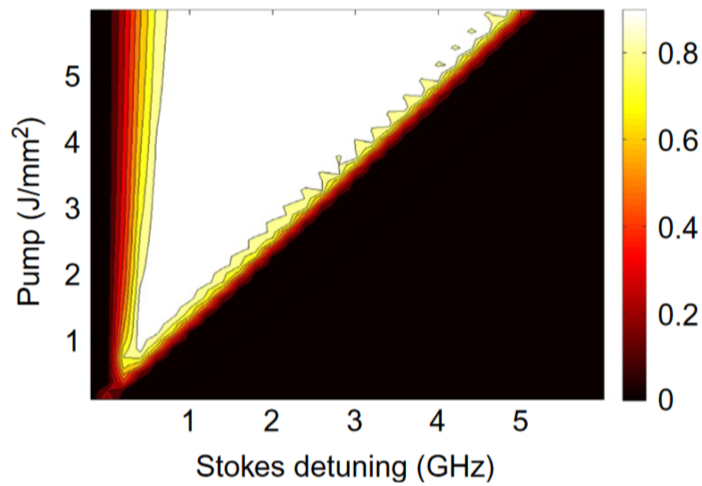

Pump E_P
Stokes E_S
Dynamic Δ
Rabi freq. Ω
Δ_0
1
2
Frac. population
$N_{v=1}$ / $N_{v=0}$
10
5
0.5
0
1
0.5
–8
–6
–4
–2
0
2
4
6
8
10
Time (ns)

Simulation of SARP showing complete population transfer from H2 ($v = 0, J = 0$) to H2 ($v = 1, J = 2$) using partially overlapping nanosecond pump, Ep (top panel), and Stokes, ES, pulses (arbitrary units). The middle panel shows the dynamic detuning Δ (GHz) and the Raman Rabi frequency Ω (GHz) in the presence of a pump pulse (fluence 2 J/mm^2 and duration 7 ns) partially over lapping with a Stokes pulse of fluence 0.5 J/mm^2 and duration of 5 ns. Δ_0 is the zero-field detuning. The bottom panel shows Stark-induced adiabatic population inversion as a fraction of the total population, when resonance (Δ = 0) is crossed in the presence of a strong Rabi coupling frequency Ω.

SARP is a Threshold Phenomenon

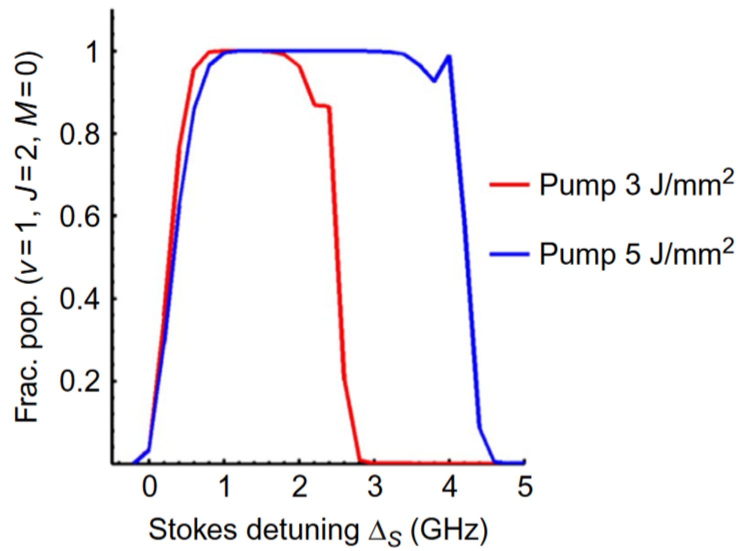


Fractional population transfer from $H_2(v=0, J=0)$ *to* $H_2(v=1, J=2, M=0)$ *as a function of the pump fluence for various zero-field Stokes detunings.*

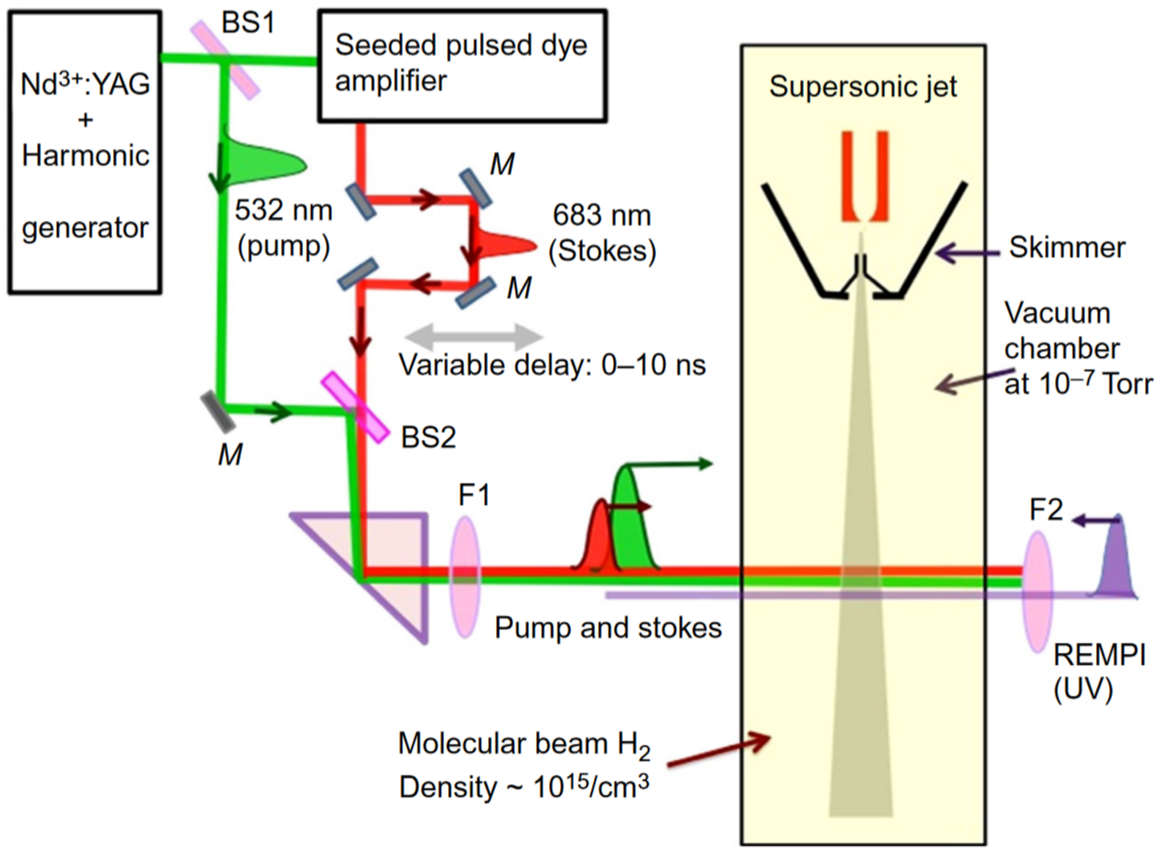


Contour map of fractional population transfer to the target $H_2(v=1, J=2, M=0)$ *level as a function of the pump fluence and the zero-field Stokes detuning.*

Experimental demonstation of SARP prepaping single and superpostions of quantum states



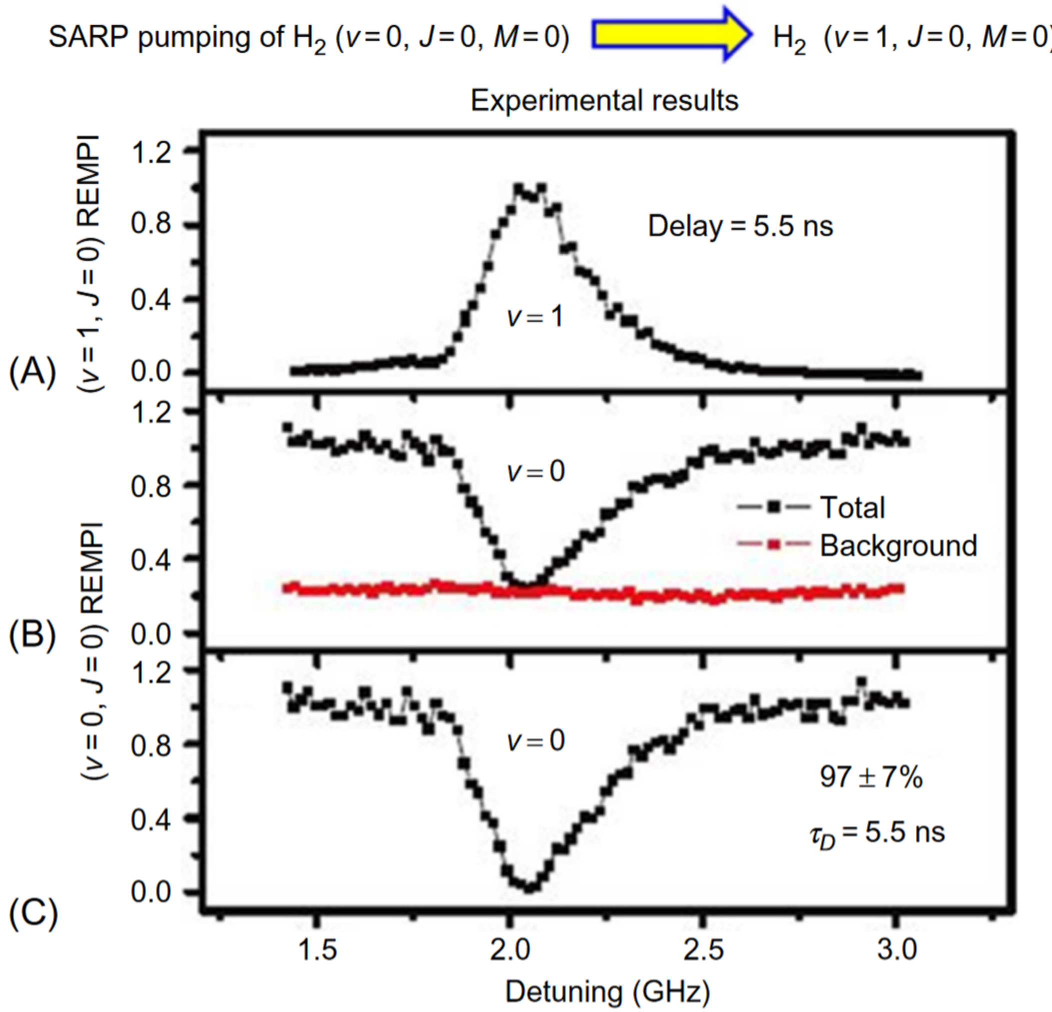
Fractional population transfer to the target $H_2(v = 1, J = 2, M = 0)$ level as a function of the Stokes detuning for two specific pump fluences. The Stokes fluence was held at a constant value of 1/4 of the pump fluence.



The delayed sequence of pump and Stokes pulses is focused onto the molecular beam using an $f = 40$ cm lens.

Preparation of a Bi-Axial Superposition State Within a Single Rovibratioinal $H_2(v = 1, j = 2)$ Eignstate

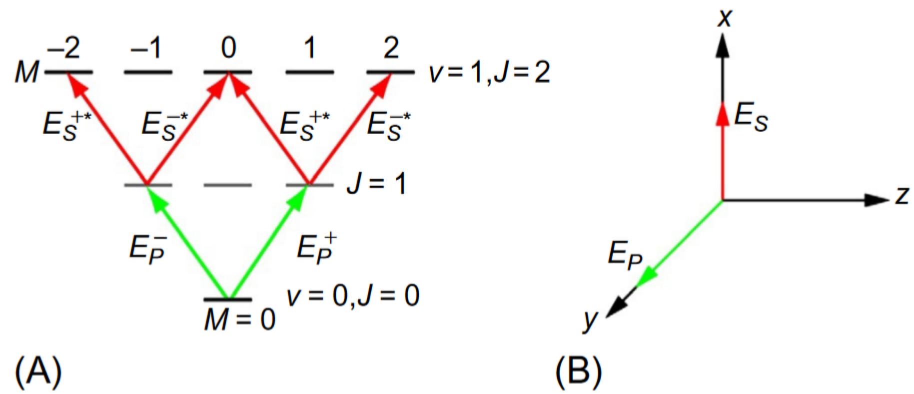
$$\Psi_{v,j} = \exp(-iE_{\nu,j}t/\hbar)\sum_{M} C_M|\nu, j, m\rangle$$



SARP pumping of H2 (v = 0, J = 0, M = 0)
H2 (v = 1, J = 0, M = 0)
Experimental results
(v = 1, J = 0) REMPI
Delay = 5.5 ns
v = 1
(A)
(B)
(C)
(v = 0, J = 0) REMPI
v = 0
Total
Background
v = 0
97 ± 7%
τD = 5.5 ns
1.2
0.8
0.4
0.0
1.5
2.0
2.5
3.0
Detuning (GHz)

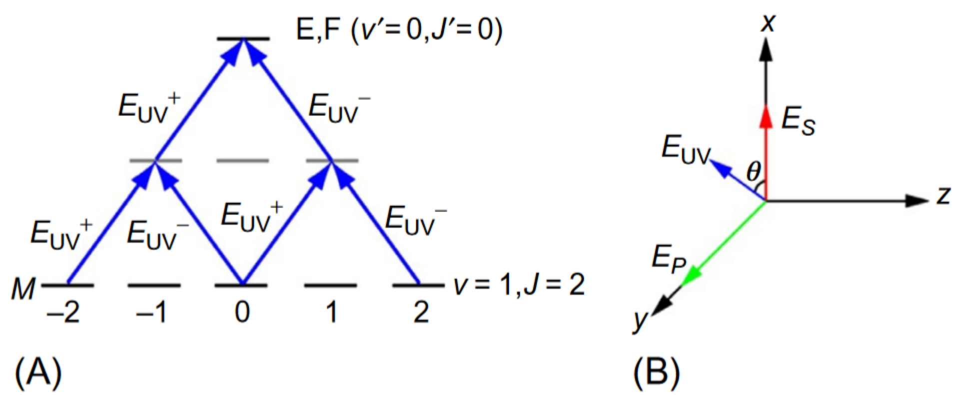
Demonstration of SARP achieving the complete population transfer from $H_2(v = 0, J = 0)$ *to* $H_2(v = 1, J = 0)$.

$$|\psi(t)\rangle = 1/\sqrt{2}[|\nu = 1, j = 2, m = -2\rangle - |v = 1, j = 2, m = +2\rangle] \tag{25}$$



(A) SARP excitation scheme used to prepare an M-sublevel superposition using left and right circularly polarized pump and Stokes laser pulses. The left and right circularly polarized components of the optical fields are derived from the linearly polarized transverse pump and Stokes waves as described in the text. (B) Molecular center-of-mass coordinate system with the z-axis oriented along the laser propagation direction.

$$E_P^+ = i\frac{E_P}{\sqrt{2}};\ E_P^- = i\frac{E_P}{\sqrt{2}};\ E_S^+ = -\frac{E_s}{\sqrt{2}};\ E_S^- = \frac{E_s}{\sqrt{2}}$$

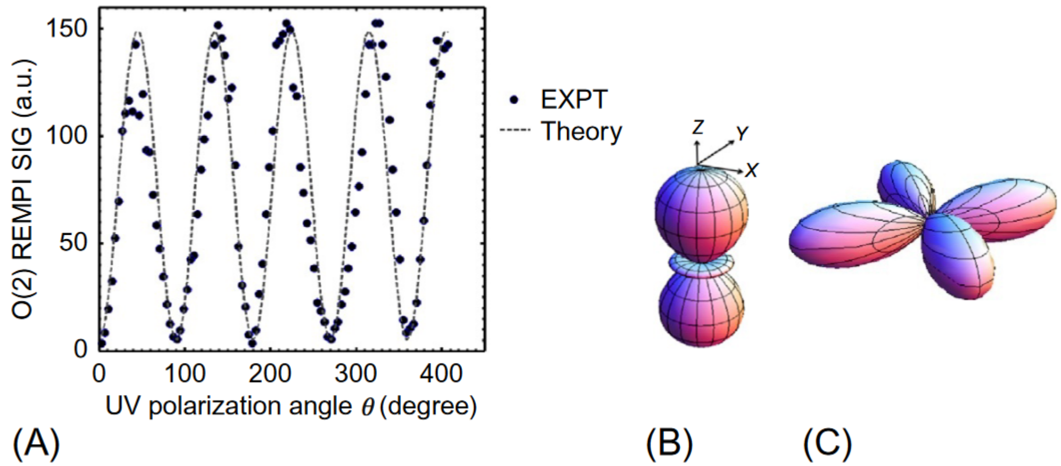


(A) (2 + 1) O(2) REMPI excitation scheme to detect M-sublevel coherence using polarized UV laser pulses. The left and right circular components of the UV laser polarization are derived from the linear polarization. (B) Rotated polarization direction of UV laser optical field relative to the direction (x) of the Stokes laser field. All laser beams propagate parallel to the quantization z-axis.

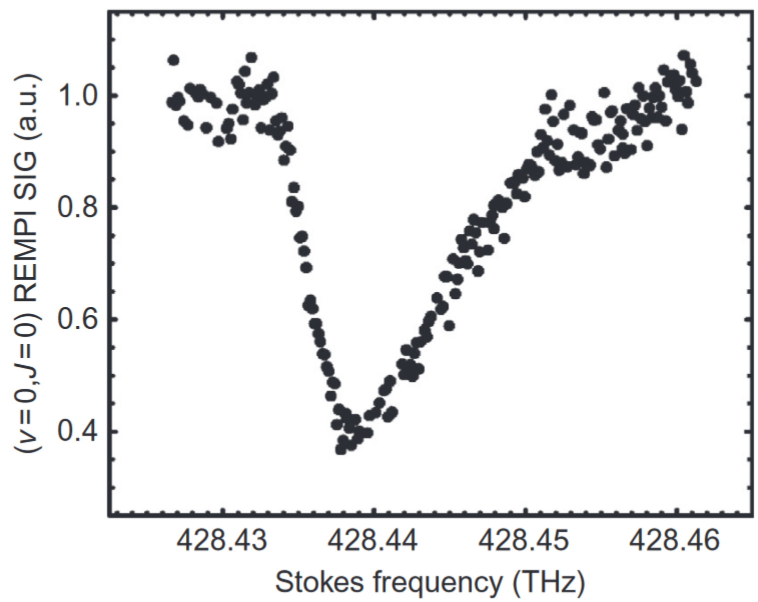
$$\mathrm{O}_2 \propto \left| C_- {E_{UV}^+}^2 + \sqrt{\frac{2}{3}} C_0 E_{UV}^+ E_{UV}^- + C_+ {E_{UV}^-}^2 \right|^2 \tag{27}$$

$$E_{UV}^+ = -\frac{E_{UV}}{\sqrt{2}} \exp[-i\theta]; \quad E_{UV}^- = -\frac{E_{UV}}{\sqrt{2}} \exp[-i\theta] \tag{28}$$

Demonstration That SARP is Robust Technique for Preparing a Desired Rovibartional M-Quantum State



(A) E, F1Σ + g v0 = 0, J0 = 0 ð X1 ÞΣ + g v = 1,J = 2 ð O(2 Þ) REMPI signal from H2 (v = 1, J = 2) excited state prepared by SARP with cross polarized pump and Stokes laser pulses. The REMPI signal is plotted against the polarization direction (angle θ) of the UV laser relative to the direction of the Stokes polarization (x). (B) 3-D polar plot of the angular momentum polarization with alignment parameters A 2 ðÞ 0 = 1 and A 2 ðÞ = 0, calculated using the fitted values of the M-state amplitudes. (C) Biaxial distribution of rotor axes.



Depletion of the Q(0) E,F1Σ + g v0 ¼ 0, J0 ¼ 0 ð X1 ÞΣ + g v ¼ 0,J ¼ 0 ð RE ÞMPI signal as a function of Stokes laser frequency in THz. The depletion of the REMPI signal calibrates the population transfer from the ground H2 (v ¼ 0,J¼ 0) ! H2 (v ¼ 1,J¼ 2) level.