Multiphoton population transfer between rovibrational states of HF: adiabatic rapid passage in a diatomic molecule

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Abstract
Efficient population transfer by adiabatically chirping through a multiphoton resonance in microwave driven and kicked Rydberg atoms has recently been reported both experimentally and theoretically. Here we report on our simulations in which we have exploited this mechanism to vibrationally excite a diatomic molecule up to $|v = 4, J\rangle$ from the ground state by chirping through a four-photon resonance condition. This is an efficient means of population transfer, which is an alternative to the ladder climbing scheme requiring chirping through a sequence of states in the correct order. We discuss and compare one-dimensional quantum and classical models where there is no rotational degree of freedom. This comparison suggests that for the lowest laser intensity we consider, the process is classically forbidden and the transition occurs through tunnelling. We show that for larger peak intensities, the transfer can be looked upon as a classical transition in phase space, similar to that observed in the atomic case. We extend our simulations to fully three-dimensional quantum calculations and investigate the effect of coupling between different rotational pathways. We finally discuss the effect of thermal averaging over the initial $J$-states using a temperature for which the first few rotational levels inside the $\nu = 0$ manifold are populated.

1. Introduction

Since femtosecond lasers became available in laboratories, creation of vibrationally excited molecules has led to important discoveries and applications. Apart from the fundamental physics aspect of these studies, steering chemical reactions emerged as a practical application since unlikely chemical reaction paths can become favoured by the excitation of certain rovibrational levels. Particularly, a large body of work has been devoted to the dissociation of small molecules using femtosecond lasers (see [1, 2]). Break-up of large molecules can also be controlled by the excitation of a particular rovibrational mode, which puts efforts devoted to the studies of selective vibrational excitation next to those towards dissociation [3–9]. The main methodology for exciting the vibrational states of molecules has been vibrational ladder climbing where the driving laser pulse is chirped through a series of single-photon resonances in order to transfer population into a desired final state. Short durations of femtosecond lasers have provided relatively large spectral bandwidths, which can potentially contain many frequencies desired to adapt to the vibrational evolution of the molecule.

A more recent use of vibrationally excited molecules is in quantum information science [10]. The possibility of implementing well-known classical algorithms using the effects of quantum interference relies on the availability of Bohr-like non-dispersing wave packets whose unitary evolution in time is necessary to perform computations. Such wave packets require near equally spaced energy levels in order to endure decoherence. One way this has been realized is by exposing very highly excited Rydberg atoms ($n \sim 300$) to a series of impulsive electric field kicks [11]. The fact that the difference in energy spacings between adjacent $n$-manifolds scales like $\sim 1/n^3$ means the energy change is $2/n$ times the energy spacing itself (given that energy scales $\sim 1/(2n^2)$). For $n = 300$, this translates into a change in energy that is $1/150$ of the energy of $n = 300$. This has been observed to be small enough for such highly excited Rydberg wave packets to survive for several Rydberg periods before...
incoherence starts to become important. Short periods of vibrational oscillations and similarities to a harmonic oscillator make vibrationally excited molecules a potential candidate to be used in such studies. For example, a recent study has utilized vibrationally excited iodine molecules to perform an ultrafast discrete Fourier transform by tailoring a vibrational wave packet coupled to an electronic transition [12].

An efficient method of population transfer in a Li atom between its highly excited Rydberg states has been experimentally realized [13] by adiabatically chirping a microwave pulse through a ten-photon resonance condition. Starting from a state with the principle quantum number \( n = 72 \), they experimentally observed \( \sim 80\% \) population transfer into the \( n = 82 \) manifold. The physical mechanism behind the process has been explained in terms of a quantum ten-photon transition (multiphoton adiabatic rapid passage) or equivalently by a classical transition in phase space [14] through classical and quantum simulations for microwave-driven [14] and kicked Rydberg atoms [15].

In this work, we utilize the same multiphoton adiabatic rapid passage mechanism [13, 14] to excite a ground-state diatomic molecule into a rovibrational excited state. Using HF as an example, we are able to simulate complete population transfer from the ground vibrational state \( |v = 0, J \rangle \) into the \( |v = 4, J \rangle \) manifold by chirping an IR laser through a four-photon resonance condition. The previously studied atomic cases and the molecular case studied in this work differ in the sense that the molecule starts in the ground vibrational state with the smallest possible classical action, while the Rydberg sense that the molecule starts in the ground vibrational state, \( \nu_{0} = \sqrt{\frac{\alpha}{2mD}} \), and the number of bound states can be deduced from

\[
N_{\text{bound}} = \frac{\alpha}{2mD} < 1.2. \tag{3}
\]

For these sets of parameters, we have found that \( \nu < 21.7 \) meaning that 21 bound states exist in the vibrational spectrum of HF in the absence of any external field.

The interaction Hamiltonian describing the effect of the applied driving pulse is \( -\mathcal{F}(t)\mu_{e} \), where we use a Gaussian carrier envelope as opposed to a flat-top envelope as in [15]:

\[
\mathcal{F}(t) = F_{IR} \exp \left[ -\left( \frac{\Delta t}{\Delta t_{0}} \right)^{2} \right] \cos(\omega t + \phi_{0}) \tag{4}
\]

The peak field strength \( F_{IR} \) is proportional to the square-root of the laser intensity \( \sim \sqrt{I} \). The central frequency \( \omega \) of the transition is \( \Delta E/N_{\text{phot}} \), where \( \Delta E \) is the energy difference between the ground state of HF and that of the targeted final state, and \( N_{\text{phot}} \) is the number of photons needed for the resonance condition. For the four-photon resonance condition we study below, \( \omega = 0.0168 \) au, which falls into the far
Figure 1. Time-dependent evolution of the probability $P$ to find the HF molecule in vibrational states with $v = 0–4$ for the four-photon resonance excitation from the ground state $v = 0$ to $v = 4$. The IR pulse has a peak intensity of $5 \times 10^{13}$ W cm$^{-2}$ and the carrier envelope centred at $t = 0$ ps has a width of 1.38 ps at FWHM.

The infrared region of the electromagnetic spectrum. The chirp range for the laser field is $\omega = 2s_0/\tau_s$ with $s = 0.02 - 0.04$ resulting in a change in central frequency by 2–4%. Time steps taken during the propagation of the Schrödinger equation are chosen such that there are roughly 44 time points in each cycle of the infrared pulse. Time runs from $-t_0$ to $t_0$ which centres the peak of the carrier envelope at $t = 0$. We use the dipole function $\mu(r)$ for HF from [18] having the form $\mu(r) = A r \exp(-B r^2)$ with $A = 0.4541$ and $B = 0.0064$.

We evaluate the probability for finding the molecule in a given vibrational state by projecting the field-free eigenstates of HF onto the time-dependent wavefunction. These eigenstates are generated on the same radial mesh used in a previous calculation [45].

Figure 1 shows the time-dependent probabilities to find the HF molecule in vibrational manifolds $v = 0–4$ when it starts out in the $v = 0$ state and is driven up to $v = 4$ through the four-photon resonance condition. The driving intensity is $5 \times 10^{13}$ W cm$^{-2}$ and the carrier envelope is $\sim 1.38$ ps at FWHM. The laser pulse is chirped from 2% of the four-photon resonance frequency below to 2% above the field-free resonance condition. The initial state $v = 0$ is completely depleted and the entire population ends up in $v = 4$. Although the intermediate states get populated during the transition at roughly 20–40% level, they all transition up to $v = 4$ after the pulse is turned off. For instance, at around 1 ps, the entire population is essentially in either $v = 3$ or $v = 4$ state, and $v = 3$ transitions into $v = 4$ at $\sim 2$ ps. This is a direct consequence of the fact that the vibrational period changes little with energy and the anharmonicity of the vibrational energy levels is engrossed inside the chirp plus the bandwidth of the carrier envelope.

Instead of chirping through a multiphoton transition, if we wanted to transfer the population via a ladder climbing scheme like the one used in [4], we would have to induce a series of single-photon transitions: $0 \rightarrow 1, 1 \rightarrow 2, 2 \rightarrow 3$, and finally $1 \rightarrow 4$ starting from $v = 0$. The resonance frequency of the $0 \rightarrow 1$ transition would be needed to be decreased to keep up with the evolving vibrational distribution. In this scenario involving HF, we would have to chirp the $0 \rightarrow 1$ transition frequency down by more than $\sim 14\%$ of its initial value to reach up to $v = 4$. Compared to the 2% chirp we needed as shown in figure 1, this is a relatively large chirp.

The peak intensity used in figure 1 is the lowest intensity at which we could get the system to transfer with 100% efficiency for the aforementioned pulse duration and chirp. Table 1 lists the final probabilities to find the system in $v = 0$ and $v$ states for various peak intensities $I$, chirp ranges and carrier envelope widths in units of classical vibrational periods $\tau_M$ corresponding to that of $v = 0$. Decreasing the peak intensity used in figure 1 by a factor of 5 down to $1 \times 10^{13}$ W cm$^{-2}$ results in only $\sim 4\%$ transition probability into $v = 4$, and rest of the population stays in the initial $v = 0$ state. Note that this only corresponds to a decrease in the peak field strength by a factor of $\sim 2.2$. At this point, doubling the carrier envelope width roughly doubles the final yield in $v = 4$, and the entire population still resides in states with $v = 0$ and 4. Further doubling the pulse width gives another factor of $\sim 2$ in the final population inside the $v = 4$ state. Having quadrupled the carrier envelope width up to 672 fs, decreasing the peak field intensity by a factor of 2 again reduced the final population inside $v = 4$ by roughly a factor of 25 down to $\sim 1\%$. Lengthening the pulse width to 1344 fs only gives a factor of 2 boost. In the case of the 672 fs pulse, doubling the chirp range from 2% to 4% also gives a factor of 2 drop in the final yield. In this very last case shown in table 1 where the chirp range is twice the size compared to a previous case with the same intensity and pulse width, $\sim 2\%$ of the population goes up to $v = 3$ after the pulse intensity drops down by about 4 orders of magnitude towards the end of the pulse. This is a three-photon transition which is swept through during chirping over a larger frequency range close to the end of the pulse. In all the other cases in table 1, the entire population resides either in $v = 0 \text{ or } v = 4$.

For the transitioning depicted in figure 1, the magnitudes of the one-dimensional wavefunction in space at different points in time along the IR pulse envelope are plotted in fig 2. At half the peak intensity $2.5 \times 10^{13}$ W cm$^{-2}$ before the transition (figure 2(a)), the system is entirely in the initial $v = 0$ state. This roughly corresponds to $t = -1.12$ ps in figure 1 when $\sim 5\%$ of the population is in the $v = 1$ state and the remaining $\sim 95\%$ is in the initial state. At the

**Table 1. Probabilities $P$ to find HF in vibrational states with $v = 0$ and $v = 4$ for various intensities $I$ (W cm$^{-2}$), chirp ranges and widths of the carrier envelope ($\tau_M$) in units of classical oscillation period $\tau_M$ of $v = 0$ for the one-dimensional quantum model discussed in the text.**

<table>
<thead>
<tr>
<th>$I$ (W cm$^{-2}$)</th>
<th>Chirp</th>
<th>$\tau_M$ (ps)</th>
<th>$P_{v=0}$</th>
<th>$P_{v=4}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$5 \times 10^{13}$</td>
<td>2%</td>
<td>168</td>
<td>0.00</td>
<td>1.00</td>
</tr>
<tr>
<td>$1 \times 10^{13}$</td>
<td>2%</td>
<td>168</td>
<td>0.93</td>
<td>0.07</td>
</tr>
<tr>
<td>$1 \times 10^{13}$</td>
<td>2%</td>
<td>336</td>
<td>0.87</td>
<td>0.13</td>
</tr>
<tr>
<td>$1 \times 10^{13}$</td>
<td>2%</td>
<td>672</td>
<td>0.75</td>
<td>0.25</td>
</tr>
<tr>
<td>$5 \times 10^{12}$</td>
<td>2%</td>
<td>672</td>
<td>0.99</td>
<td>0.01</td>
</tr>
<tr>
<td>$5 \times 10^{12}$</td>
<td>2%</td>
<td>1344</td>
<td>0.97</td>
<td>0.02</td>
</tr>
<tr>
<td>$5 \times 10^{12}$</td>
<td>4%</td>
<td>672</td>
<td>0.97</td>
<td>0.006</td>
</tr>
</tbody>
</table>

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3
with mixing coefficients using microwaves has been explained in [14] using a one-dimensional classical model. Since the transition is induced by chirping through a multiphoton resonance in the quantum picture, it is natural to expect that a well-defined sharp final state distribution would not result in the classical picture which lacks resonance concept. Surprisingly, authors observed that initial state distribution would not result in the classical picture which they investigated the classical mechanism responsible for the transition. Although there are no resonances in the classical picture, they found that microwave driving creates a stable island centred at roughly halfway between the initial and final states in classical action, which corresponds to $n$ for the Coulomb problem. The initial state just below the island and the final state above it form a separatrix at the right field strength. Driving the system a little harder destroys the separatrix and creates a chaotic sea, mixing the trajectories that were initially on the initial stable surface (i.e. initial state) into the chaotic sea. This narrow chaotic sea also borders the stable surface above the island of stability. During the falling edge of the driving pulse, the field strength becomes small enough so that the stable surfaces again form the separatrix and the initial final stable surfaces, which trap the trajectories that were mixed into the chaotic sea. By chirping the microwave frequency a small amount, most of the trajectories can be made to end up on the stable surface above the island of stability. In this section, we will demonstrate that the same separatrix crossing mechanism is also responsible for the vibrational population transfer observed in section 2.1.

In our classical simulations, we solve Hamilton’s equations in one dimension using a fourth-order adaptive step-size Runge–Kutta method. We use the same Hamiltonian used in the one-dimensional quantum simulations except that we now use the $x$-coordinate instead of the radial coordinate with the same numerical parameters $x_0$ and $\alpha$. The interaction Hamiltonian is again $-\mathcal{F}(t)\mu$, where $\mu(x) = Ax \exp(-Bx^2)$ with $A = 0.4541$ and $B = 0.0064$ as before, and the IR laser is polarized along the $x$-direction. The corresponding classical force from the Morse potential is

$$-\frac{dV_M(x)}{dx} = 2D\alpha\left[e^{-\alpha(x-x_0)}-2e^{-\alpha(x-x_0)^2}\right]. \quad (5)$$

Figure 3 shows the final $v$-distribution of the transition probabilities for the four-photon resonance condition starting
from the ground state. An IR pulse with a carrier envelope of \( \sim 1.38 \) ps at FHWM is used with a chirp range of 2\% for various peak field intensities. We use 500 trajectories for each peak intensity and bin the final energy of the trajectories in \( \nu \) after the IR pulse is turned off. We bin the population in \( \nu \) according to equation 2 such that it is rounded off to the nearest integer. The squares in figure 3 are for \( I = 5 \times 10^{13} \) W cm\(^{-2} \), the stars are for \( I = 9 \times 10^{13} \) W cm\(^{-2} \), the circles are for \( I = 13.5 \times 10^{13} \) W cm\(^{-2} \), and the triangles are for \( I = 18 \times 10^{13} \) W cm\(^{-2} \). The square with \( 5 \times 10^{13} \) W cm\(^{-2} \) peak intensity corresponds exactly to the one-dimensional quantum case presented in figure 1 and surprisingly shows peak intensity corresponds exactly to the one-dimensional spread of final \( \nu \) that covers from \( -1/2 \) to \( 1/2 \). The classical action \( I \) is the angle variable which runs from \( 1/2 \) to \( 1 \). In this case, there is no spread in the final \( \nu \)-distribution, a behaviour also displayed classically using Rydberg atoms in our previous work [14].

Increasing the peak intensity to \( 13.5 \times 10^{13} \) W cm\(^{-2} \) (circles) results in a final \( \nu \) spread that covers from \( \nu = 3 \) to 7 with about half the population residing in \( \nu = 4 \). Further increase in the peak intensity to \( 18 \times 10^{13} \) W cm\(^{-2} \) (triangles) widens the spread of final \( \nu \) and results in roughly 10\% dissociation (final \( E > 0 \)). In this case, \( \sim 34\% \) of the population ends up in \( \nu = 4 \) and \( \sim 19\% \) stays in the initial state.

In order to probe the classical process taking place during the transition, we looked at one-dimensional surfaces of section plots in classical phase space as described in our previous work with microwave-driven and kicked Rydberg atoms [14, 15]. We use the action-angle variables \( I \) and \( \theta \) to picture the classical phase space. They are derived in [19] for the field-free Morse potential and are given by

\[
I = 2\pi (\nu + 1/2) \\
\theta = \frac{1}{2\pi} \text{sgn}(p) \cos^{-1}\left[\frac{z + E/D}{\sqrt{1 + E/D}}\right],
\]

where \( z = \exp[-\alpha(r - r_0)] \). Here \( p \) is the momentum, \( \text{sgn}(p) \) is the sign of the momentum, and \( \theta \) is the angle variable which runs from \( -1/2 \) to \( 1/2 \). The classical action \( I \) corresponds to the quantum number \( \nu \), and tracking it in the phase space gives a clear picture of the evolution of the effective quantum number \( \nu \) as the pulse is swept through. Since the energy is a function of \( \nu + 1/2 \) (equation 2), the smallest action is \( -1/2 \) and we use \( \nu \) instead of action in our plots for clarity. The angle coordinate \( \theta \) is a measure of the phase of the classical orbit.

Figure 4 shows the surfaces of section plots for the peak IR intensities of \( 9 \times 10^{13} \) W cm\(^{-2} \) (column 1) and \( 18 \times 10^{13} \) W cm\(^{-2} \) (column 2) before (panels A1 and A2), on (panels B1 and B2), and after (panels C1 and C2) the peaks of the carrier envelopes. These intensities correspond to stars and triangles seen in figure 3 except that in figure 4 we do not chirp the frequencies in order to simplify the classical picture. On top of each surface of section, we plot the phase space positions of the trajectories at corresponding instances during the IR pulse (large filled circles). Before the transition, trajectories reside on the initial stable surface of \( \nu = 0 \) (panels A1 and A2). These correspond to intensities \( 5 \times 10^{13} \) W cm\(^{-2} \) and \( 10^{14} \) W cm\(^{-2} \) respectively. As the peak intensities of \( 9 \times 10^{13} \) W cm\(^{-2} \) and \( 18 \times 10^{13} \) W cm\(^{-2} \) are reached in B1 and B2, this stable surface is destroyed and the trajectories that were on this surface are mixed into the chaotic sea. Note that for the smaller peak intensity in B1, trajectories stay almost perfectly along the lines that are used to make up the separatrix, even after these surfaces are destroyed by the driving field. More than half of the trajectories mixed into the chaotic sea have swung around the main island of stability. In B2, where the driving field is stronger by a factor of \( \sim 1.4 \), the trajectories drift and disperse inside the chaotic sea more rapidly compared with A2, resulting in a final wider spread in \( \nu \) than in A1, as depicted by the triangles in figure 3. The fact that \( \nu \) initially has the lowest possible value at \( -1/2 \) results in the formation of a stable island centred at \( \sim -0.3 \) rad (seen more prominently in B1). This island is destroyed in B2 due to the stronger driving field. During the falling edges of the IR pulses with \( I = 5 \times 10^{13} \) W cm\(^{-2} \) and \( I = 10 \times 10^{13} \) W cm\(^{-2} \) (C1 and C2 respectively), stable surfaces are formed again and the trajectories are captured onto final stable \( \nu \)-manifolds. In C1, this means that about half the trajectories end up on the \( \nu = 4 \) surface and the other half stay on the initial \( \nu = 0 \) stable surface. A large spread of final \( \nu \) is seen in C2 in agreement with the triangles in figure 3.

3. Quantum calculations in three dimensions

A detailed account of our fully three-dimensional quantum calculations has been given in [14] for the case of a microwave-driven Rydberg atom. The difference in the molecular case is only in the radial part of the Hamiltonian describing the vibrational potential and in the dipole coupling as a function of \( r \). The details of the Morse potential and the proper dipole function used in the interaction Hamiltonian for HF were described in section 2.2 for the one-dimensional treatment of the problem. The interaction Hamiltonian itself now couples \( J \) to \( J \pm 1 \) since it is now \(-\mathcal{F}(t)\mu \cos(\theta)\). In this way, the three-dimensional calculations take into account the role of the rotational levels as they are coupled with the vibrational degree of freedom as a result of the interaction with the IR laser pulse.

Figure 5 shows time-dependent probabilities in vibrational states with \( \nu = 0 \) through \( \nu = 4 \) (panel (a)), along with the probabilities in the rotational modes \( J = 0 \) through \( J = 4 \) (panel (b)). The peak IR laser intensity, chirp range and carrier envelope width are identical to those used in the one-dimensional quantum simulations presented in figure 1. The molecule starts in the initial rovibrational state of \( | \nu = 0, J = 1 \rangle \) and is driven up to \( | \nu = 4, J = 1 \rangle \) through the four-photon resonance condition. The time evolution and the final distributions of the vibrational manifolds are very similar.
to those seen in the one-dimensional quantum simulations with the entire population transitioning into the $v = 4$ manifold after the IR pulse is turned off. This suggests that the coupling into different rotational pathways is not significantly important for the transition to occur. The probabilities for the rotational quantum numbers evolving in time seen in figure 5(b) suggest that the final rotational mode of the molecule is the one that it started out with i.e. $J = 1$. Only $J = 0$ and $J = 2$, i.e. the adjacent rotational modes get significantly excited during the transition, which transition back into $J = 1$ by the end of the IR pulse. Recall that the transition at this peak intensity stems from tunnelling as we inferred by comparing the one-dimensional quantum and classical simulations.

Population distributions in quantum numbers $v$ and $J$ before, on and after the peak of the carrier envelope are seen in figure 6. These snapshots are taken at the same instances during the IR pulse as the one-dimensional wavefunction plots seen in figure 2. At half the peak intensity (leftmost panel), the entire population is in the initial $|v = 0, J = 1\rangle$ state, similar to the one-dimensional wavefunction plot in figure 2(a). At the peak of the laser pulse (middle panel), the population has spread out and now spans $J$ up to 3 and $v$ up to 5. It is confined mostly in $v = 0, 3$ and 4 which can also be seen from figure 5(a). The probabilities display a checkerboard pattern for $J \geq 2$; for $J = 2$, $v = 0, 2$ and 4, and for $J = 3$, $v = 1, 3$ and 5 being populated. This comes from the fact that each absorbed photon can change the angular momentum by one unit and successive $v$ are roughly separated by one photon. This is different than the atomic case where the four-photon frequency would correspond to roughly the energy of the state that lies approximately half way between the initial and final states [14, 15]. After field intensity drops back to half the peak value again (rightmost panel), the entire population settles into the final $|v = 4, J = 1\rangle$ state.

The conservation of the initial rotational quantum number $J$ after the transitioning can potentially make this method appealing over the ladder climbing scheme in research involving self-imaging of molecules in strong laser fields (see [20] for a detailed account). In this context, self-imaging of a molecule by its own ionized rescattering electron in a strong laser field requires a fair level of alignment of the molecule itself in order for structural information to be recoverable.
better visibility of smaller structures in the distribution. During the
transition takes place. (left panel), during (middle panel) and after (right panel) the
vibrational states may be desirable for this type of research
from the ionization spectrum. Having molecules in excited
vibrational states may be desirable for this type of research
since the main aim is to watch and steer chemical reactions in real time. Once aligned, vibrational excitation through
ladder climbing would destroy the alignment since it would
smear the J-distribution of the aligned population. This can
be circumvented if the multiphoton adiabatic rapid passage
scheme is used to vibrationally excite the molecule after it is
aligned, preserving the alignment.

4. Thermal distribution of rotational levels

The three-dimensional quantum simulations in figure 5 show
complete population transfer into the final |ν = 4, J = 1⟩
state from the ground |ν = 0, J = 1⟩ state by chirping
through a four-photon resonance condition. This would
be experimentally challenging to achieve. In the previous
section, we have started from a well-defined specific eigenstate
|ν = 4, J = 1⟩ and drove the transition up to another specific
final eigenstate. In real-world experiments, the initial state
would be smeared over a spectrum of rotational eigenstates as
a result of non-zero temperature. In this section, we take into
account the effect of this thermal mixing of the initial states
on the population transfer. We perform the same calculations
as those in section 3 for a series of initial states |ν = 0, J⟩ for
J up to 5 and drive the same four-photon resonance condition
using the same chirp range as before. We then average the
time-dependent probabilities P_J as

\[ P = \frac{\sum_J (2J + 1) e^{-\epsilon_j/k_B T} P_J}{\sum_J (2J + 1) e^{-\epsilon_j/k_B T}}. \]

Here \( \epsilon_j \) is the energy of the eigenstate |ν = 0, J⟩ relative to
the ground state |ν = 0, J = 0⟩, \( k_B \) is the Boltzmann constant
and \( T \) is the temperature. We pick 150 K as the temperature,
which gives substantial rotational population up to \( J = 4 \) for
HF. Much lower but still experimentally feasible temperatures
as low as \( \sim 14 \) K leave the entire ensemble in the \( J = 0 \)
ground state for HF. The initial spread in \( J \) at 150 K can be
seen from the time-dependent probability distribution in
figure 7(b) at \( t = -3 \) ps. It is also plotted as the open squares
in figure 8.

Similar to figure 6, figure 7 shows the time evolutions
of probabilities for \( \nu \) (panel (a)) and \( J \) (panel (b)) quantum
numbers. Compared with figure 6(a), figure 7(a) shows that
\( \sim 10\% \) of the population stays in \( \nu = 0 \) and the remaining
\( \sim 90\% \) transitions into \( \nu = 4 \) by the end of the pulse. In this
case, \( \nu = 3 \) lingers around a little longer compared to the
pure eigenstate case in figure 6(a). Figure 7(b) shows that
states with \( J = 1, 3 \) and 4 stay roughly at the same level of
occupation as they started out with, and states with \( J = 0 \) and
\( J = 2 \) end up with same probabilities after the pulse is
turned off. In other words, roughly \( 10\% \) of the population in
\( J = 2 \) transitions into states with \( J = 0 \). The change in the
overall \( J \)-distribution as a result of the transition can be seen in
figure 8. The triangles depict the population distribution over
the rotational quantum number \( J \), and the squares represent the
initial thermal distribution inside the \( \nu = 0 \) manifold.

Another issue of concern in experiments would be the
spatial profile of an actual IR laser pulse. Since the laser
intensities of interest are in the strong field regime, most

Figure 5. (a) Same as figure 1 but from a full three-dimensional simulation with the same set of parameters as those used in the one-dimensional simulations of section 2.2. The HF molecule starts from the |ν = 0, J = 1⟩ state and is driven up to |ν = 4, J = 1⟩ through the four-photon resonance condition. (b) Time-dependent evolution of \( P \) for \( J \) up to 4. (J = 4 is the dot-dashed curve at the bottom which we did not label to prevent cluttering.) Although \( J = 0 \) and \( J = 2 \) are significantly populated during the pulse, the molecule stays entirely in \( J = 1 \) after the IR pulse is turned off.

Figure 6. (ν,J)-distributions for the run presented in figure 5 before (left panel), during (middle panel) and after (right panel) the transition takes place. \( P \) is multiplied by 5 in the middle panel for better visibility of smaller structures in the distribution. During the transition, \( \nu < 6 \) and \( J \) remains less than 4.

Figure 7. Same as figure 6 but for 150 K, where \( J = 0 \) is the ground state and the others are excited states.
likely the laser would need to be focused, resulting in a Gaussian beam profile, for instance. As table 1 indicates, the transition is sensitive to the peak laser intensity. For instance, while $1 \times 10^{13}$ W cm$^{-2}$ results in essentially no transfer at all, twice that would yield complete population transfer into $v = 4$. This suggests that in a Gaussian beam, only a small region around the focus would contribute to the transfer, other regions resulting in no transitioning at all. The final averaged picture would qualitatively look like figure 5(a) given that rotational pathways do not play a significant role in how much transfer is attained in each $v$-manifold. The amount that transitions into $v = 4$ would only weakly depend on how sharply the laser is focused since the transition occurs quite suddenly when a particular laser intensity is reached, as seen from table 1.

5. Conclusions

We have presented results of our simulations that show complete population transfer between the ground vibrational state of HF and its $v = 4$ excited state by adiabatically chirping through a four-photon resonance condition. This is a demonstration of efficient and robust population transfer in a diatomic molecule which is different from the conventional ladder climbing scheme which has been previously studied. The current method is different than ladder climbing in the sense that it does not involve chirping through a series of intermediate states in a correct order in order to transfer population [4]. The mechanism behind the population transfer is physically identical to that seen in microwave-driven and kicked atoms in the context of population transfer between Rydberg states [13–15].

One-dimensional quantum and classical models show that entire population can be excited up to $v = 4$ from the ground state by chirping through a four-photon resonance condition. The chirp required for this is not essential to the physical mechanism, but rather it serves to increase the efficiency of the population transfer. Surprisingly, we also observed that although a peak intensity of $5 \times 10^{13}$ W cm$^{-2}$ results in complete transfer into $v = 4$ in the quantum mechanical model, classical model requires at least a peak intensity of $\sim 9 \times 10^{13}$ W cm$^{-2}$ for any transition to occur. This suggests that the complete population transfer in the quantum case with $5 \times 10^{13}$ W cm$^{-2}$ is classically forbidden and happens through tunnelling. For peak laser intensities of $9 \times 10^{13}$ W cm$^{-2}$ and higher, we observe the same separatrix crossing mechanism observed in Rydberg atoms for the multiphoton population transfer. Although $I = 9 \times 10^{13}$ W cm$^{-2}$ results in perfect final-state resolution, intensities up to twice as high result in substantial final state spreads and even dissociation.

By extending our simulations to fully three-dimensional quantum calculations, we introduced the effect of rotational coupling in the excitation process for the four-photon transition from the $|v = 0; J = 1\rangle$ to $|v = 4; J = 1\rangle$ state of HF. Again, we observed complete transfer of population into the final $v = 4$ manifold, but this time we also demonstrated that the transferred population entirely retained $J = 1$ character after the IR pulse is turned off. The $J$-states that played a significant role during the transition are only the adjacent $J = 0$ and $J = 2$ states. In order to simulate a more realistic experimental condition, we considered a case where the initial state is not a single rovibrational eigenstate of the field-free HF molecule, but rather a thermal distribution of initial states. We have particularly chosen 150 K as our temperature since this gives a sizable spread in $J$ up to $J = 4$ inside the $v = 0$ manifold of HF. For the same set of IR
pulses and chirp ranges used in the one-dimensional and three-dimensional simulations, we have seen that the total fraction of the population transferred into $\nu = 4$ decreased by only $\sim 10\%$, and that the final $J$-distribution only differs than that in the beginning of the laser pulse for $J = 0$ and $J = 2$ by roughly $5\%$.

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References