Impact of Pulse Polarization on Coherent Vibrational Ladder Climbing Signals

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**ABSTRACT:** We report a theoretical study that elaborates the influence of the polarization state of both the pump and the probe pulse in ultrafast coherent vibrational ladder climbing experiments in the mid-infrared. Whereas a subensemble in a randomly oriented sample of molecules is excited by the pump pulse in this multiphoton process, further inhomogeneities such as the spatial profile of the laser beams, the longitudinal attenuation in the sample, and the probe beam polarization have to be taken into account. Analytical expressions for a density function describing the number of molecules that are exposed to an effective pump intensity are introduced, and the variation of the population distribution and the actual transient absorption signal in dependence on the polarization-state combinations for pump and probe pulse are discussed in detail. In simulations on the model system carboxy-hemoglobin, it is demonstrated that the polarization states play important roles both for exciting a certain population distribution and for actually observing it. In particular, it will be discussed under which conditions experimental data indicates a population inversion.

**INTRODUCTION**

In nonlinear ultrafast spectroscopy, the polarization states of the involved laser pulses and their relative orientation play an important role, and their systematic variation allows the inference of valuable information on the molecule under study. For instance, in condensed-phase transient absorption spectroscopy using two linearly polarized pulses, rotational relaxation can be monitored by measuring the anisotropy, which often is expressed as a monoeponential but may also take more complex forms depending on the orientation of the transition dipole and the symmetry of the system. Further contributions arising from, e.g., a nonstationary solvent bath can be elucidated with anisotropy studies employing a pump–dump–probe sequence having a circularly polarized pump pulse. Also in pump–probe spectroscopy, changing the pump polarization from linear to circular can be beneficial, e.g., to separate overlapping signals or identify magnetic dipole–field interactions. However, to avoid any contribution arising from the orientation of the molecules, the probe polarization is commonly set to the magic angle (θma = 54.74°) relative to the pump polarization. This procedure is analogous to (generally non-time-resolved) fluorescence anisotropy measurements where an analyzer is oriented under the magic angle with respect to the polarization of the excitation field.

For processes of higher order, the polarization effect may become even more pronounced. Whereas a linearly polarized pump pulse creates a $\cos^2 \theta$ distribution in case of a one-photon excitation (with θ being the angle between the light polarization and the direction of the absorbing dipole), in a two-photon excitation process the distribution takes the form of $\cos^2 \theta$, also giving rise to a larger maximum anisotropy value. This effect can be partially reduced by using circularly polarized pump pulses. A very strong dependence on the ellipticity of the laser pulse can be found in (gas-phase) high-order multiphoton ionization. Reiss showed that the cross section for multiphoton ionization generally is much smaller in the case of circular polarization than in the case of linear polarization. Two intuitive reasons are (i) the different number of possible transitions due to angular momentum selection rules, and (ii) the amplitude of the electric field vector, which is smaller by a factor of $\sqrt{2}$ compared to the maximum of a linearly polarized electric field with identical temporally averaged intensity (see, e.g., discussion in ref 7). This circumstance is also observed in high-harmonic generation, where the yield strongly drops with increasing ellipticity of the fundamental beam’s polarization.

Whereas the aforementioned processes comprise electronic transitions, multiphoton excitation is also exploited in coherent...
vibrational ladder climbing with femtosecond laser pulses in the mid-infrared (MIR). To reach higher-lying vibrational levels, MIR pulses with a downchirp (i.e., high frequency components precede lower ones in the pulse) are more effective,12–16 since the chirp accounts for the shrinking transition frequencies of the anharmonic potential (Figure 1). Beyond ladder climbing in relatively small molecules, coherent vibrational efficiency in carboxyhemoglobin (HbCO)16 was realized. In theoretical studies, it has been derived that even higher vibrational states than the \( v = 6 \) observed in ref 16 should be accessible in HbCO, with significant population inversion.17–19 Kühn20 showed that CO ligand dissociation in HbCO by vibrational climbing seems hardly possible, in contrast to metal—carbonyl complexes where ground-state photolysis of a CO ligand in, e.g., Cr(CO)615 was demonstrated. Yet, appropriately shaped MIR pulses are expected to excite the vibrational motion in HbCO more efficiently than linearly chirped ones,18 an approach rendered possible due to recently developed techniques for direct MIR pulse shaping.21–23

In this paper, we explore to what extent the polarization state of the MIR pump pulses influences the signals observed in vibrational ladder climbing. Compared to multiphoton ionization, condition (ii) concerning the peak intensity of a circularly polarized pump is the same, but the selection rule criterion (i) is not applicable in an analogous way for ladder climbing. Hence, the population distribution in the different levels and the ability to achieve and observe a population inversion between two of them may strongly depend on the polarization state of the pump pulse. However, also for linearly polarized pump and probe pulses, the combined effect originating from the relative orientation of the polarizations is important for a prediction of population distributions and inversion, as will be elaborated in the following.

## DESCRIPTION OF THE MODEL

**Molecular System.** We consider the case of vibrational ladder climbing in HbCO as experimentally demonstrated in a study with linearly polarized pump pulses16,17 from which several parameters can be adopted. The ground-state absorption of the vibration of Fe-bound CO is at 951 cm\(^{-1}\), while the Morse potential exhibits an anharmonicity of \(-1.28\%\), i.e., subsequent transitions differ by 25 cm\(^{-1}\). The transition dipole moments are well described by the harmonic approximation in which they increase like \((v + 1)^{1/2}\) for the vibrational levels \(v\). The dephasing time \(T_2\) for all levels was measured as 1.6 ps.

The measured relaxation times are known to be about 1 order of magnitude greater than \(T_2\) and to be shorter for higher vibrational levels. However, since these values are much longer than the pulse duration, their exact values do not strongly alter the result just after the excitation, thus we used a constant value \(T_2 = 25\) ps in the simulations.

The HbCO molecules are assumed to be randomly distributed in solution. Rotational effects do not contribute to the signals for two reasons: first, the protein hemoglobin has a rotational diffusion time of 26 ns in aqueous solution,24 so that the protein can be regarded as nonmoving on the time scales considered here; second, the orientation of the CO transition dipole moment is only slightly displaced from the heme normal,25 and anisotropy measurements with infrared pump and probe pulses confirm the rigid CO orientation within the protein.25,26 Theoretical modeling further predicts that, even for highly excited CO, the direction of the transition dipole does not (or only slightly) change.18

The multiphoton excitation in vibrational ladder climbing, a strong-field process going beyond the perturbative approximation, is modeled by a numerical Runge—Kutta integration of a Bloch model27 comprising 18 vibrational levels (12 levels for the plots of Figures 4–6, where only low intensities and the three lowest levels are considered), which is implemented in the Matlab software environment.28 From the population distribution derived for 100 intensity values (1000 for Figure 7), we calculate the change in transmission of the probe pulse. The different intensity values are needed to take into account the spatial properties of both pump and probe pulses as outlined in the following sections.

As a side note, it should be mentioned that HbCO offers two possibilities for coherent vibrational ladder climbing: one for Fe-bound CO as considered here, and one for photolyzed CO in the primary docking site of the heme pocket,29–31 where population relaxation times are even larger by more than an order of magnitude, but the absorption strength is lower by about the same amount.

**Laser Pulses.** In our model, which is a generalization of the discussion in ref 16, the randomly oriented HbCO proteins are excited by a MIR femtosecond pump with either linear or circular polarization, and monitored by a femtosecond probe. Both beams travel collinearly, have identical diameters and exhibit a Gaussian spatial profile of the form

\[
I(I_0, r, z) = \frac{2}{\pi w_0^2} I_0 e^{-2r^2/w_0^2 - \alpha_0 z}
\]

with the beam waist \(w_0\), the distance \(r\) from the beam center, the distance \(z\) into the sample. The electric field in the spectral domain, we use

\[
E(\omega) = \frac{1}{2} \hat{\epsilon}(\omega - \omega_0) = \frac{1}{2} |\hat{\epsilon}(\omega - \omega_0)| e^{i\varphi(\omega - \omega_0)}
\]

with the spectral phase \(\varphi(\omega)\) and the complex-valued spectral envelope \(\hat{\epsilon}(\omega)\). For a purely linear chirp, the spectral phase takes the form \(\varphi(\omega) = (1/2)b_2 r_2 \omega_2^2\), with the second-order spectral phase coefficient \(b_2\) which leads to a downchirped pulse for \(b_2 > 0\), and to an upchirped one for \(b_2 < 0\), respectively. The electric field in the time domain is given as

\[
E(t) = \mathcal{F}[E(\omega)] = \hat{\epsilon}(t) e^{-i\omega_0 t}
\]
Figure 2. The two coordinate systems used in this publication. The laser propagates from left to right. A general direction is indicated in red to define the angles. For linearly polarized pump pulses (left), the angle \( \theta \) is measured with respect to the pump polarization direction. For circularly polarized pump pulses (right), \( \theta \) is measured with respect to the wave vector \( \mathbf{k} \) and \( \phi \) in the plane where the field vectors of pump and probe lie. The dotted arrow along the circle indicates that the pump field vector is rotating around the propagation direction.

where \( \mathcal{T} \) stands for the Fourier transform. The complex-valued temporal envelope \( \mathcal{E}(t) \), is related to the spectral domain via \( \mathcal{T}^{-1}[\mathcal{E}(\omega)] = \mathcal{E}(\omega) \).

We define the pulse area\(^3\) as

\[
A = \frac{\mu}{\hbar} \int_{-\infty}^{\infty} \mathcal{E}(t) \, dt = \frac{\mu}{\hbar} \mathcal{E}(\omega = 0) \tag{4}
\]

where \( \mu \) is the transition dipole moment between states \( \nu = 0 \) and \( \nu = 1 \), so that the pulse area for a transform-limited (TL) pulse is \( A = \mu/\hbar \mathcal{E}(\omega = 0) \), whereas for a pulse with spectral phase modulation, we get \( A = \mu/\hbar \mathcal{E}(\omega = 0) e^{i\omega(t_0-b)} \). Thus, the absolute value of the pulse area, \( |A| \), is the same for all spectral phase modulations. Since the spectral intensity does not change either when a spectral phase is applied, we define our pulse intensities in units of the pulse area, e.g., a pulse intensity of \( \pi \) means that \( |A| = \pi \). It should be noted that as we do not have one but many transition frequencies, the pulse area is defined here with respect to \( \omega_0 \) and not to the ground-state absorption frequency. Hence, a \( \pi \) pulse will not lead to half a Rabi oscillation of the lowest transition \( \nu = 0 \rightarrow \nu = 1 \).

The pump pulse spectra are Gaussians centered at \( \tilde{\nu}_0 = 1890 \text{ cm}^{-1} \) (so that the lowest transition is actually not excited by the most intense wavenumber) with a full width at half-maximum (fwhm) of 150 cm\(^{-1} \). We will consider both TL and chirped pump pulses. Effective ladder climbing was found for a downchirped MIR pump pulse with \( b_2 = -32000 \text{ fs}^2 \),\(^1\) which was also assumed in our simulations. The duration of these pulses is below 1 ps, short compared to the population relaxation characteristics of HbCO.

In ref 16, the population distribution was probed 16 ps after the temporal center of the pump pulses. To allow a comparison, all the population distributions in this publication also correspond to a delay of 16 ps. For the transient absorption data, a probe pulse arrives with a delay of 16 ps relative to the pump pulse. Whereas the spatial intensity distribution and polarization of the probe pulse are explicitly included in the following, its duration (and hence finite spectral width) is neglected, and any transition frequency can be probed.

In order to investigate differences for linear and circular pump polarization, we describe the interaction in spherical coordinates, with the polar axis oriented along the pump polarization direction in the case of linear pump polarization (left coordinate system of Figure 2), and along the direction of propagation in the case of circular pump pulses (right coordinate system of Figure 2), respectively.\(^2\) If \( \theta \) is the angle between the molecule’s dipole and the polar axis, effective intensities depending on the angle \( \theta \) emerge for both pump and probe pulses, which together with eq 1 can be expressed as

\[
F_{\text{eff}}(l_0, r, z, \theta, \phi) = f(l_0, r, z)f(\theta, \phi) \tag{5}
\]

with a function \( f(\theta, \phi) \) taking into account the relative orientation of the dipoles and the electric field vector. For linearly polarized pump and probe beams, one gets

\[
f_{\text{pu}}(\theta, \phi) = \cos^2 \theta \tag{6}
\]

\[
f_{\text{pr}}(\theta, \phi) = \frac{1}{2} \sin^2 \theta \tag{7}
\]

\[
f_{\text{pe}}(\theta, \phi) = \sin^2 \theta \cos^2 \phi \tag{9}
\]

where \( f_{\text{pu}}(\theta) \) is isotropic in the plane perpendicular to the propagation direction, and the direction of the probe polarization can be chosen arbitrarily in this plane.

**Transient Absorption Signal.** In an experimental pump–probe experiment, three main sources of inhomogeneity will contribute to the transient absorption signal. Hence, we have to include them in our simulation in order to adequately describe those signals. Inhomogeneity (a) arises from the orientation of the molecules which are both pumped and probed, which is represented by the dependence on the angles \( \theta \) and \( \phi \). Inhomogeneity (b) is due to the Gaussian beam profile of pump and probe beams, represented by the \( r \) dependence. Because of the multiphoton character of the process, the central part of the probe beam will monitor the population of higher-lying levels generated by the most intense part of the pump pulse, while further away from the beam center, the molecules will exhibit less excitation. Inhomogeneity (c) covers the longitudinal attenuation of the beams when they traverse the sample, as is represented by the \( z \) dependence.

The \( r, z, \) and \( f(\theta, \phi) \) dependence is included in the absorption change interaction with the pump pulse by using the effective intensity (eq 5)

\[
\Delta \alpha(f_{\text{pu}}, r) = \Delta \alpha(l_{\text{pu}}, r, z, f_{\text{pu}}(\theta, \phi), r) \tag{10}
\]

The appearance of \( r \) takes into account that the absorption change will not be constant after the excitation process at \( \tau \approx 0 \).

The probability of molecules (whose orientation is given by \( \theta \) and \( \phi \)) to be probed by the linearly polarized probe pulse is given by \( f_{\text{pr}}(\theta, \phi) \). In order to calculate the transient absorption signal, we will look at the absorption of the probe pulse in the pump-excited sample (which is indicated by the superscript \( x \)):

\[
\frac{d \alpha_x(l_{\text{pr}}, r, z, \tau)}{d \epsilon} = -(\alpha_0 + \Delta \alpha(f_{\text{pr}}(\theta, \phi), \nu_0, \phi))f_{\text{pr}}(l_{\text{pr}}, r, z, \tau) \tag{11}
\]
with the average
\[
\langle \Delta \alpha (I_{pr}, \tau) f_{pr}(\theta, \phi) \rangle_{0, \theta, \phi} = \frac{\int_{0}^{2\pi} \int_{0}^{\pi} \Delta \alpha (I_{pr}, \tau) f_{pr}(\theta, \phi) \sin \theta \ d\theta \ d\phi}{\int_{0}^{2\pi} \int_{0}^{\pi} f_{pr}(\theta, \phi) \sin \theta \ d\theta \ d\phi}
\]
(12)
whose denominator takes the value 4\pi/3. By separation of variables and subsequent integration, eq 11 can be rewritten to
\[
\ln I_{pr}^{\alpha}(I_{0,pr}, r, L, \tau) = - \int_{0}^{L} \left( \alpha_{0} + \langle \Delta \alpha (I_{pr}^{\alpha}, \tau) f_{pr}(\theta, \phi) \rangle_{0, \theta, \phi} \right) dz
\]
(13)
and if both sides are taken as arguments of exponential functions, we arrive at
\[
I_{pr}^{\alpha}(I_{0,pr}, r, L, \tau) = I_{pr}^{\alpha}(I_{0,pr}, r, 0) e^{-\alpha_{0}L} e^{-\int_{0}^{L} \langle \Delta \alpha (I_{pr}^{\alpha}, \tau) f_{pr}(\theta, \phi) \rangle_{0, \theta, \phi} dz}
\]
(14)
where the superscript nx stands for the case when there is no excitation by the pump.

To make a further analytical description possible, it is assumed that the change in transmitted probe intensity is small and the approximation \( e^{x} \approx 1 + x \) can be used. Hence, we can rewrite eq 14:
\[
I_{pr}^{\alpha}(I_{0,pr}, r, L, \tau) = I_{pr}^{\alpha}(I_{0,pr}, r, 0) \left( 1 - \int_{0}^{L} \langle \Delta \alpha (I_{pr}^{\alpha}, \tau) f_{pr}(\theta, \phi) \rangle_{0, \theta, \phi} \right) dz
\]
(15)
The \( r \) dependence is removed by integrating the spatial intensity profile in polar coordinates, which yields
\[
I_{pr}^{\alpha}(I_{0,pr}, r, L, \tau) = I_{pr}^{\alpha}(I_{0,pr}, 0, L) - \int_{0}^{L} \int_{0}^{2\pi \tau} \Delta \alpha (I_{pr}^{\alpha}, \tau) f_{pr}(\theta, \phi) I_{pr}^{\alpha}(I_{0,pr}, r, L) \ d\theta \ d\phi \ d\tau \ d\theta \ d\phi
\]
(16)
From eq 1, we know that \( I_{pr}^{\alpha}(I_{0,pr}, L) = I_{0,pr} e^{-\alpha_{0}L} \), and in combination with eq 12, the averaged difference of the Napierian absorption coefficient seen by the probe pulse can be derived:
\[
\Delta \alpha (I_{0,pr}, \tau) \approx \frac{I_{pr}^{\alpha}(I_{0,pr}, 0, L, \tau) - I_{pr}^{\alpha}(I_{0,pr}, 0, L, \tau)}{I_{pr}^{\alpha}(I_{0,pr}, 0, L, \tau)}
\]
(17)
This expression takes into account the inhomogeneities \( a_{r,c} \). Since different molecules see different \( I_{pr}^{\alpha} \), it is worthwhile to reformulate eq 17 in terms of an equivalent to a “density of states” in dependence on \( I_{pr}^{\alpha} \). For varying polarization of the pump beam, the number of molecules being excited with a certain \( I_{pr}^{\alpha} \) will not be the same. Thus, we define
\[
\eta = e^{-2\tau/\omega} - \alpha_{0} f_{pu}(\theta, \phi)
\]
(18)
so that \( I_{pr}^{\alpha} = (2/\pi \omega^{2})\eta I_{0,pu} \). Hence, eq 17 takes the form
\[
\Delta \alpha (I_{0,pu}, \tau) = \frac{3}{\pi \omega^{2} \tau L} \int_{0}^{L} \int_{0}^{2\pi} \int_{0}^{\pi} \Delta \alpha \left( \frac{2}{\pi \omega^{2}} \eta I_{0,pu}, \tau \right) f_{pr}(\theta, \phi) \sin \theta \ e^{-2\tau/\omega} \ d\theta \ d\phi \ d\tau \ d\theta \ d\phi
\]
(19)
and the value \( \eta_{\text{max}} \) is 1 for a linear pump and 1/2 for a circular one, as is evident from eq 6 and eq 8.

This procedure can be regarded as follows: let us assume we have a homogeneous excitation with a pump intensity \((2/\pi \omega^{2})\eta I_{0,pu}\) causing a differential absorption signal. Depending on \( \eta \), the number of probed molecules that are actually excited by the pump varies, therefore we have to weigh the signal with a density function \( g(\eta) \). For instance, the molecules which see the maximum intensity \( (\eta = \eta_{\text{max}}) \) must be located at \( r = 0 \) and have the optimal orientation, which is true only for very few molecules so that \( g(\eta_{\text{max}}) \) must approach zero. Equation 19 integrates over all accessible intensities, resulting in the averaged absorption change.

The density function \( g(\eta) \) can be calculated analytically. In order to get an impression on the different nature of \( g(\eta) \) for the various polarization states, only a very thin layer is regarded, so that the \( z \) dependence in the \( \delta \)-function of eq 20 can be neglected. If we further substitute \( u = \eta f_{pu}(\theta, \phi)e^{-2\tau/\omega} \), it simplifies to
\[
g(\eta) = \frac{3}{4\pi} \int_{-\infty}^{\infty} \int_{0}^{2\pi} \int_{0}^{\pi} \left[ \Theta [f_{pu}(\theta, \phi) - \eta] f_{pr}(\theta, \phi) \sin \theta \right] d\theta \ d\phi \ du
\]
(21)
with the Heaviside function \( \Theta \). By substitution of \( u = f_{pu}(\theta, \phi) - \eta \) and partial integration with respect to \( u \), we get the density function
\[
g_{\text{lin}}(\eta) = 3(1 - \sqrt{\eta}) \left[ \cos^{2} \xi + \frac{1 - \sqrt{\eta}}{2\sqrt{\eta}} \sin^{2} \xi \right]
\]
(22)
\[
g(\eta) = 3(1 - \sqrt{\eta})
\]
(23)
\[
g_{\perp}(\eta) = 3 \left( \frac{\sqrt{\eta}}{2} + \frac{1}{2\sqrt{\eta}} - 1 \right)
\]
(24)
\[
g_{\alpha}(\eta) = 1 - \frac{1}{3} g(\eta) + \frac{2}{3} g_{\perp}(\eta)
\]
(25)
\[
g_{\text{c}}(\eta) = 3 \sqrt{1 - 2\eta}
\]
(26)
for the general case of two linearly polarized pulses with an angle \( \xi \) between the polarization directions, the special cases with parallel (\( || \)) and perpendicular (\( \perp \)) linear polarizations for pump
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Figure 3. The function $g(\eta)$ for the three different polarization combinations considered here.

and probe, the magic angle case where $\cos^2 \xi = 1/3$, and the case with circular pump and linear probe polarization ($o$), respectively. All functions $g(\eta)$ are normalized, i.e., $\int_0^{\eta_{\text{max}}} g(\eta) \, d\eta = 1$, even though $g_o(\eta)$ is divergent for $\eta \rightarrow 0$.

In the case of two circularly polarized beams, $g_o(\eta)$ is reproduced, because as soon as the pump polarization is circular, the collinearly propagating probe sees a distribution which is isotropic in the plane perpendicular to the propagation direction, independent of its own polarization state. A further possibility, a linear pump and a circular probe polarization, leads to

$$g_j(\eta) = \frac{1}{2} [g_o(\eta) + g_\perp(\eta)]$$

which is equivalent to $\xi = 45^\circ$. The latter case is somewhat special if the $z$-dependence of the probe pulse is additionally considered, because in case of an anisotropic excitation, the circular probe pulse is attenuated inhomogeneously and picks up a linearly polarized component.

It should be noted that the situation with a circularly polarized pump and a linearly polarized probe pulse does not give the result that is equivalent to an isotropic distribution, because the pump cannot excite dipoles oriented along the propagation direction. Cho$^4$ has shown that this problem can be circumvented by introducing an angle of $90^\circ - \varphi_{\text{ma}}$ between the propagation directions of pump and probe. However, this case will not be discussed in this study.

## RESULTS AND DISCUSSION

**Density Functions.** The density functions derived in the previous section clearly differ for the three cases considered in this paper (Figure 3). For an interpretation, we first look at the region around $\eta \approx 1$. The density functions reflect how many of the probed molecules are excited by a high effective intensity. In the case of perpendicular polarizations, this value is much smaller than for parallel ones, which basically reflects the probe polarization’s impact on the obtainable pump–probe signal. The opposite effect is observed for $\eta \approx 0$: for parallel polarizations, there is a finite amount of probed molecules that basically do not see the pump field, whereas this situation occurs for the vast majority of molecules in the perpendicular case.

![Figure 4](image)

**Figure 4.** Polar plots of the population distribution of the three lowest levels for three different intensities of the linearly polarized pump pulse. The columns correspond to level $v = 0$ to $v = 2$ (from left to right), and the rows correspond to intensities of $0.1 \pi^2$, $\pi^2$, and $3 \pi^2$ (from top to bottom). The pump beam is propagating in the $z$-direction, is polarized along the $y$-direction, and is downchirped. The color represents the actual population, rescaled from the minimum (blue) to the maximum (red) value.

![Figure 5](image)

**Figure 5.** Polar plots of the population distribution of the three lowest levels for three different intensities of the circularly polarized pump pulse. The columns correspond to level $v = 0$ to $v = 2$ (from left to right), and the rows correspond to intensities of $0.1 \pi^2$, $\pi^2$, and $3 \pi^2$ (from top to bottom). The pump beam is propagating in the $z$-direction, is polarized circularly in the $xy$-plane, and is downchirped. The color represents the actual population, rescaled from the minimum (blue) to the maximum (red) value.

All curves have their maximum at $\eta = 0$ which is a consequence of the existence of molecules whose axis is oriented in the propagation direction. As a sidenote, the curves at $\eta = 0$ exhibit another interesting aspect: $g_o(0)$ is divergent, $g_j(0)$ is not but its slope is, and $g_\perp(0)$ as well as its derivative are finite values.

Taking a closer look at $g_o(\eta)$, we see that it is only defined up to $\eta = 1/2$, which is a direct consequence of $\eta_{\text{max}}$ following from
eq 8, and also is equivalent to criterion (ii) from multiphoton ionization. For \( \eta \approx 0.45 \), the density exceeds the ones for linear polarizations.

With regard to vibrational ladder climbing pump–probe experiments, these observations allow an intuitive prediction: for the generation and subsequent observation of highly excited molecules, parallel polarizations are most appropriate.

**Population Distribution.** In a first step, we want to leave out the probe pulse and only look at the population distribution after the excitation by the pump pulse in dependence on its polarization. Three-dimensional plots showing the populations in the three lowest levels for three different intensities are displayed in Figure 4 and Figure 5 for linear and circular pump polarization, respectively.

At the lowest intensity, only a small fraction is excited at all and hence the \( v = 0 \) population resembles a sphere (top left graph in Figure 4 and Figure 5). The \( v = 1 \) level (top middle) has a \( \cos^2 \theta \) shape in the linear, and a donut shape (with \( \cos^2 \theta \) lateral cut) in the circular case. The \( v = 2 \) level (top left) accordingly has a \( \cos^4 \theta \) and donut (with \( \cos^4 \theta \) lateral cut) shape, respectively, very similar to what is found in two-photon induced fluorescence.\(^5\)

![Figure 6](image1.png)

Figure 6. Cuts in the \( yz \)-plane through the population distribution of the three lowest levels for linear (left column) and circular (right column) pump pulses.

![Figure 7](image2.png)

Figure 7. The population of the first 12 levels of the vibrational ladder as a function of pump pulse intensity (in multiples of \( \pi^2 \)), as it would be derived from an experiment with pump and probe pulses that are both linearly polarized and parallel (solid line), or circularly and linearly polarized (thin line), respectively. In panel a, the pump pulse is down-chirped. It is TL in panel b, and up-chirped in panel c.

At the medium intensity (middle row), significant portions of the \( v = 0 \) population have been excited to higher levels, so that a donut and dumbbell-like distribution remain in the ground-state, respectively (middle left). In the \( v = 1 \) (center graph) and \( v = 2 \)
(middle right) states, there is significantly more population, and also the shape of the structures is jolted compared to the low intensity. Since the perturbative regime is not applicable anymore, saturation effects contribute so that along a disadvantageous direction the same amount of molecules may be excited as in an optimally oriented direction because more molecules can still be found in the lower state.

This is further confirmed by the distribution corresponding to the high intensity (bottom row). The $v = 0$ population gets even flatter in the case of the linear pump pulse and resembles a donut shape (bottom left in Figure 4), or more constricted for the circular pump pulse with the dumbbell shape (bottom left in Figure 5), respectively. At this intensity, also the $v = 1$ populations exhibit the same trend: for the linear pump pulse (bottom middle in Figure 4), molecules oriented along the $y$-direction are efficiently excited to higher-lying states, and hence the initial $\cos^2 \theta$ distribution changes to a diabolo-like shape, which is symmetric with respect to the $y$-axis, i.e., the direction of the pump polarization. For the circular pump pulse (bottom middle in Figure 5), the initial donut shape is constricted and will also become similar to a diabolo, but symmetric with respect to the $z$-axis, if the intensity is increased even further.

Looking at the $v = 2$ population for circular pump polarization (bottom right in Figure 5), one can see that two effects lead to the jolted shape: molecules oriented in the plane perpendicular to the $z$ axis are efficiently excited to higher states, taking away population from the equator direction (the polar axis is the $z$ axis). For molecules oriented in directions with small $\theta$ values, it is less likely to be excited efficiently, therefore the region close to the poles is still filled up from lower levels. These effects are also evident in Figure 6, where cuts through the population distribution for linear and circular pump pulses of different intensities are shown.

The probed population distribution strongly depends on $I_{0,pump}$. Since vibrational ladder climbing is a coherent process, population inversion over several levels can be achieved with very intense pulses. Figure 7 shows the level population as it would be derived in a pump-probe experiment in dependence on the pump pulse intensity. For rather weak pump pulses, one can see that the population of the $v = 0$ level follows a line corresponding to a $I^2$ dependence, expected in a perturbative process. For higher intensities, the strong-field regime sets in and for instance Rabi oscillations, Stark shift effects, and saturation may occur. As a consequence, the distribution is not monotonous anymore, but there may be more molecules excited to higher-lying levels than to intermediate ones.

In Figure 7, for circular pump polarization, the populations in the perturbative regime will be lower due to the smaller peak intensity than for a linear pump polarization at the same spatially and temporally averaged intensity. For the $v = 1$ level, which is mostly populated by a single-photon process, there is already a difference between the two considered polarization combinations because of the inclusion of the probe polarization direction.

Very large values are chosen for the maximum intensities of Figure 7 in order to visualize the difference between TL and chirped pump pulses. In the downchirped case (Figure 7a), higher-lying vibrational levels are reached already at lower intensities due to the frequency ordering in the pulse, and also population inversion is observed earlier. At very high intensities, the signal almost saturates, whereas for TL pump pulses (Figure 7b), one can see strong oscillations. This can be interpreted as Rabi oscillations, but not over two but all levels: after ladder climbing the TL pulse may cause a ladder descent again, followed again by climbing, and so on. For the down-chirped pulse, this is not achieved because the frequency ordering does not allow it, yet it is possible to observe it for adjacent in lieu of for all levels, as is reflected in the slight oscillatory modulation of the curves. Note that this oscillatory feature does not appear at the same intensity values for linear and circular pump polarizations. In Figure 7c, the case of an upchirped pulse is shown. Since the frequency ordering is opposite to the vibrational ladder’s
polarization combinations are indicated.

The positive signal at 1951 cm$^{-1}$ corresponds to the ground-state bleach, whereas all other positive signals to predominating stimulated emission as a result of population inversion between adjacent levels. Negative signals correspond to an absorption, i.e., for the two states separated energetically by a photon of the frequency indicated on the x-axis, the higher-lying state is less populated.

From the spectra for the lowest pump intensity (Figures 8a and 9a), one can see that the intensity is too low to achieve any population inversion. However, the spectrum for the downchirped pulse reveals that higher-lying levels are already accessible, whereas for the TL pump pulse basically no molecules are excited to $\nu > 5$. Note that the total amount of bleached molecules does not differ too much, but the number of molecules that are driven to higher levels clearly does. In the case of parallel pump and probe polarizations, more of those molecules that were efficiently excited are probed than in the case of perpendicular polarizations. The spectrum for a circular pump and a linear probe yields a probed population distribution which comprises a slightly less efficient excitation than in the case of parallel polarizations.

The spectra for a pump intensity of 3π$^2$ (Figure 8b and Figure 9b) also show this trend that the vibrational ladder climbing is most strongly reflected in the signal for parallel polarizations, whereas it is weakest for perpendicular polarizations. Looking at Figure 9b, it is evident that this intensity is not sufficient to induce a population inversion if a TL pump pulse is used. By contrast, with the downchirped pump at this intensity (Figure 8b), population inversion will be measured for parallel pump and probe polarizations, but not in the case of perpendicular polarizations. This is remarkable because the distribution of excited molecules after the pump pulse is identical in both cases: only by the choice of the probe polarization direction can a subensemble be chosen, which either exhibits a population inversion or does not.

The signal for a circular pump pulse is again worse than the one for parallel, and better than that for perpendicular polarizations, respectively. The expressions for the density functions already indicate that $g_o(\eta)$ cannot be written as a linear combination of $g_0$ and $g_\perp$ (in contrast to the case of a linear pump and a circular probe polarization (see eq 27)), and hence the probed population distribution may be completely different although both the pump pulse intensity is the same and also a linearly polarized probe is used. To illustrate this, we will look at Figure 9c, where a TL pump at an intensity of 35π$^2$ is exciting the system. At this specific intensity, a population inversion is most efficiently achieved with a circular pump pulse.

The intensity used for Figure 8c and Figure 9c are rather high, so that already a vibrational descent (compare Figure 7b) may set in, but only for the TL pump pulse. The probed populations for the downchirped pulse are very similar for the parallel and circular cases (Figure 8c) and can be understood as a population marginal, i.e., the most excited distribution achievable with pump pulses of the given spectral width and phase. This is also evident

![Figure 9. Differential spectra of the HbCO model for TL pump pulses with an intensity of (a) $\pi^2$, (b) $3\pi^2$, and (c) $35\pi^2$. The different polarization combinations are indicated.](image)
from Figure 7a, in which the solid and dashed curves approach the same value for high pump intensities. For the TL pump pulse, the descent may lead to a situation in which the circular pump pulse reaches the highest level of excitation (as, e.g., in Figure 9c). At a different intensity, also the signal of the perpendicular case may seem more efficient than the parallel one.

In Figure 8c, population inversion is observed for all three considered polarization cases. When the intensity is further raised, for all three of them the population marginal will be reached, as is evident from Figure 7a. A similar distribution is approached for upchirped pump pulses (Figure 7c). By contrast, for the TL pump pulses, not only can an alternating ladder climbing and descent be observed, but this is done in such a way that there is less population inversion than with a chirped pulse. In Figure 7b for increasing intensity, the probed populations in the different levels oscillate, but no strong population inversion is observed anymore. Only for a narrow intensity region (around the intensity where the ground-state population has its minimum value) is a strong population inversion realized with TL pulses. This confirms that vibrational climbing with chirped pulses is not only better for achieving a population inversion because of the frequency ordering, but also because a pronounced population inversion may be observed for a much broader intensity range.

**CONCLUSION**

We have presented a formalism to describe the population distribution probed in vibrational ladder climbing experiments by taking into account the spatial profile and the polarization directions of both pump and probe beams. It was shown that different populations are probed depending on the states and the relative orientation of the polarization. By simulating vibrational ladder climbing experiments in carboxyhemoglobin, we exemplarily showed under which conditions a population inversion can be observed. For downchirped pump pulses, the excitation to higher levels is more efficient, as had been reported already both theoretically and experimentally. If very high pump intensities are used, a population marginal comprising population inversion is reached.

For TL pump pulses, vibrational ladder climbing is less efficient, but at high intensities also a vibrational descent can be realized. Our simulations indicate that at high intensities, TL pulses are not as adequate to observe population inversions as chirped pump pulses. Finally, the investigation if a circular pump pulse can lead to results differing strongly from the case of a linear pump pulse has shown that population distributions are possible which cannot be created identically with a linear pump pulse. This may be useful in some special situations, however, the signal obtained with pump and probe pulses polarized linearly and oriented parallelly will contain contributions from high-lying levels already at lower pump intensities.

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**ACKNOWLEDGMENT**

We wish to thank Adeline Bonvalet, Kevin F. Lee, and Marten H. Vos for fruitful discussions. This work was supported by Agence Nationale de la Recherche (ANR-06-BLAN-0286). P.N. acknowledges financial support from the Deutsche Akademie der Naturforscher Leopoldina (BMBF-LPDS 2009-6).

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