# Selective excitation of vibrational overtones in an anharmonic ladder with frequency- and amplitude-modulated laser pulses

J. S. Melinger and D. McMorrow
*Naval Research Laboratory, Code 6613, Washington, D.C. 20375*

C. Hillegas and W. S. Warren
*Department of Chemistry and the Princeton Center for Photonics and Optoelectronics, Princeton University, Princeton, New Jersey 08544*

(Received 3 August 1994)

We show numerically that the complex hyperbolic secant pulse provides robust selective inversion of vibrational overtones. A density-matrix analysis is performed for a ten-level Morse-oscillator approximation of a diatomic molecule. We also show that in the limit of adiabatic excitation the complex-hyperbolic-secant pulse yields an inversion spectrum that is narrower than its spectral bandwidth.

PACS number(s): 42.50.Hz

## INTRODUCTION

The preparation of molecules in a selected highly excited vibrational state, or set of vibrational states is an important precursor to many chemical physics studies. Unfortunately, direct pumping of vibrational overtones from the ground level with a single laser pulse is often a difficult task because of the relatively small transition dipole moments involved. To obtain high transfer efficiency extremely intense fields are usually needed, which increases the likelihood of unwanted nonlinear processes. Furthermore, there still remains the issue of selectivity.

An alternate method for the efficient pumping of high-lying vibrational states is to transfer population sequentially up the anharmonic ladder by multiphoton absorption with broad bandwidth infrared laser pulses. Recent theoretical work has shown how specially tailored ultrashort pulses are effective in promoting population efficiently to high vibrational levels [1–4]. In one approach, pulses with an appropriate chirp (frequency sweep) transfer population to high vibrational overtones as the pulse frequency successively excites higher vibrational transitions [1,2]. Another approach uses purely amplitude-modulated pulses, and pulse sequences, which are tuned to a particular multiphoton transition [3,4]. For sufficiently strong laser fields, high overtones may be efficiently populated by direct multiphoton absorption. A problem that is associated with each of these approaches, is that neither is inherently selective in the population of high overtones. For example, while it is possible with a single purely amplitude-modulated pulse to find a specific resonance offset and Rabi frequency to selectively invert a single vibrational level [4], the degree of selectivity is not robust, but, instead, remains sensitive to the parameters of the applied laser field. In general, robustness to experimental parameters will be necessary for the successful laboratory implementation of such laser control schemes [5].

In this paper we show how the complex hyperbolic secant [the slowly varying part of the complex electric amplitude field takes the form $\varepsilon(t)=\mathrm{sech}(\alpha t)^{1+\mu i}$] can be used to selectively invert vibrational overtones in an anharmonic oscillator by sequential multiphoton absorption. We show that the selective inversion found with the complex hyperbolic secant pulse is robust with respect to the applied Rabi frequency, and, that similar robustness is not obtained with more simple linear frequency-swept pulses, and unswept pulses. Finally, we point out that the inversion spectrum of the complex hyperbolic secant pulse may be far narrower than its full spectral bandwidth, and we comment on the conditions under which such sub-pulse-bandwidth resolution is obtained.

## THEORETICAL MODEL

In this section we describe the model used to simulate population transfer dynamics in an infrared-active-diatomic molecule. A Morse oscillator model [6] is used to approximate the vibrational potential. The Morse eigenenergies are given by

$$W(v)=\omega_e(v+\tfrac{1}{2})-\omega_e x_e(v+\tfrac{1}{2})^2-D\ , \tag{1}$$

where $\omega_e$ is the oscillator frequency, $\omega_e x_e$ is the anharmonicity constant, $D$ is the dissociation energy, and $v$ is the vibrational quantum number.

The scalar component of the electric field along the bond coordinate may be written as

$$E(t)=a(t)e^{i[\omega_0 t+\phi(t)]}\ , \tag{2}$$

where $a(t)$ is a real valued pulse envelope function, $\omega_0$ is the carrier frequency of the pulse, and $\phi(t)$ is the time-dependent phase of the electric field. The instantaneous frequency of the pulse is given by

$$\omega(t)=\omega_0+d\phi(t)/dt. \tag{3}$$

The time evolution of the system is found by evaluating the equation of motion for the density operator

$$d\rho(t)/dt=(1/i\hbar)[H(t),\rho(t)], \tag{4}$$

where $H(t)=H_0+H_{\mathrm{int}}(t)$, $H_0$ is the unperturbed Hamil-

 

tonian, $H_{\text{int}}(t)$ describes the usual electric-dipole interaction of the vibrational degree of freedom with the applied laser field, and $\rho(t)$ is the density operator. In the next section we numerically evaluate the matrix elements of Eq. (4) for the hyperbolic secant pulse envelope with different functional forms for the instantaneous pulse frequency.

## RESULTS

The excitation properties of the complex hyperbolic secant pulse in a two-level system are well known from NMR and laser spectroscopy [7,8]. Figure 1(a) shows the hyperbolic secant pulse amplitude and corresponding hyperbolic tangent frequency sweep for the complex wave form $\varepsilon(t)=\text{sech}(\alpha t)^{1+5i}$. (In the following, $\tau_p$ represents the pulse width at full width at half maximum (FWHM), or $\tau_p \approx 2.6/\alpha$.) Figure 1(b) shows the inversion spectrum

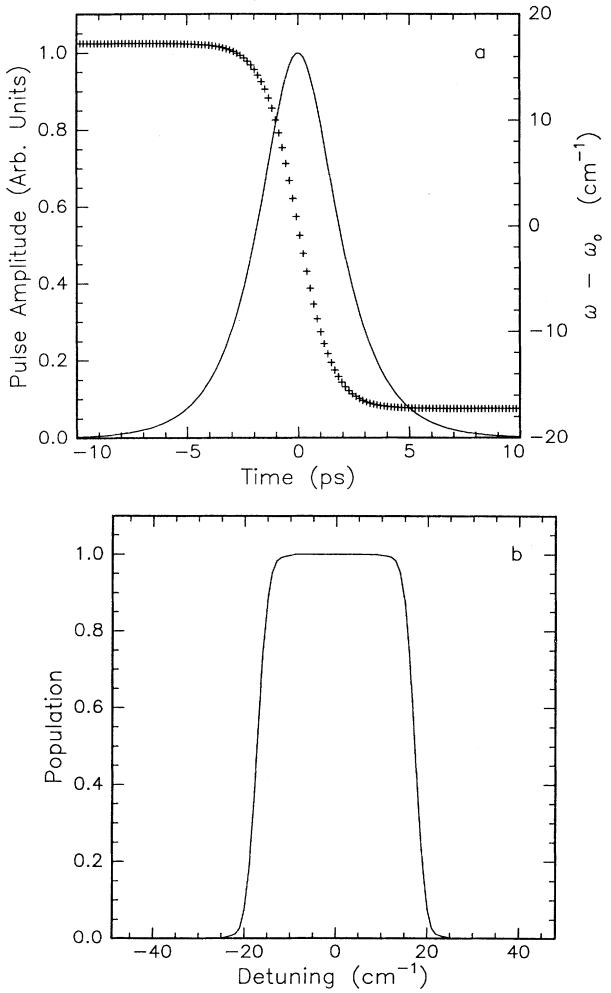


FIG. 1. (a) Pulse amplitude profile (——) and corresponding hyperbolic tangent frequency sweep (+++) of the pulse $\varepsilon(t)=\text{sech}(\alpha t)^{1+5i}$. The pulse width $\tau_p$ (FWHM) is 4 ps. (b) The near-rectangular inversion spectrum produced by the pulse in (a) for a two-level system with a peak Rabi frequency of $2\pi\times 50\ \text{cm}^{-1}$.

associated with this pulse for a two-level system when the condition for adiabatic passage is satisfied. For a two-level system, the condition for adiabatic passage may be written as [8]

$$d\theta(t)/dt \ll [\Omega^2(t)+\Delta^2(t)]^{1/2}\ , \tag{5}$$

where $\theta(t)\equiv\pi/2+\tan^{-1}[\Delta(t)/\Omega(t)]$, $\Omega(t)$ $[=\mu a(t)/\hbar]$ is the time-dependent Rabi frequency, $\Delta(t)$ $[=\omega_r-\omega_0+d\phi(t)/dt]$ is the frequency detuning from resonance, and $\omega_r$ is the transition frequency. When the inequality of Eq. (5) is satisfied the complex hyperbolic secant pulse inverts a near-rectangular profile that remains insensitive to further changes in the Rabi frequency. This robustness is inherent to the adiabatic excitation process.

We now examine the excitation properties of the following wave forms which are used to excite the multilevel anharmonic ladder:

$$a(t)=\text{sech}(\alpha t),\quad \omega(t)=\omega_0+\mu\alpha\tanh(\alpha t), \tag{6a}$$

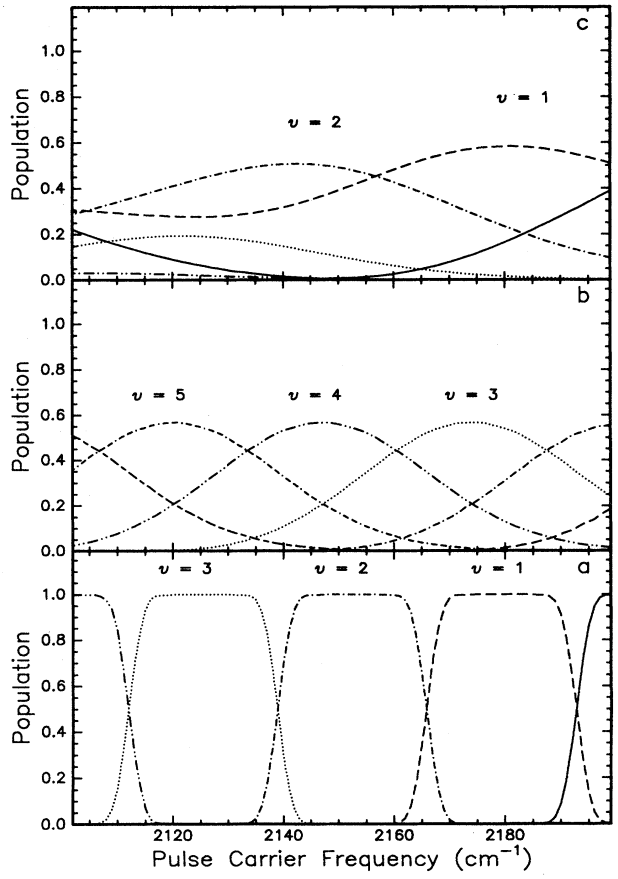


FIG. 2. The excitation spectrum associated with each of the wave forms given in Eq. (6) for excitation of the ten-level anharmonic ladder. Each curve corresponds to the population in a specific vibrational level. (a) Complex hyperbolic secant $\tau_p=4$ ps, $\mu=14.2$; (b) linearly swept hyperbolic secant $\tau_p=4$ ps, $b=9.4\ \text{cm}^{-1}/\text{ps}$; and (c) unmodulated hyperbolic secant, $\tau_p=150$ fs. The peak Rabi frequency in each case is $2\pi\times 100\ \text{cm}^{-1}$. $v=0$ (——); $v=6$ (– – –); others as labeled.

$$a(t)=\mathrm{sech}(\alpha t),\quad \omega(t)=\omega_0+2bt, \tag{6b}$$

$$a(t)=\mathrm{sech}(\alpha t),\quad \omega(t)=\omega_0. \tag{6c}$$

To construct the anharmonic ladder, vibrational parameters for the isolated CO molecule are taken from reference [9]. The CO vibrational frequency ($\omega_e$) is 2170 $cm^{-1}$, and the anharmonicity constant ($\omega_e x_e$) is 13.5 $cm^{-1}$. Equation (4) is solved for a ten-level anharmonic ladder with the system initially in the ground vibrational level. Thus, we ignore both dissociation and rotational effects. For simplicity, only transitions with $\Delta v=\pm 1$ are considered, and all transition moments are set equal. In each example where frequency swept pulses are used the pulse frequency sweeps from blue to red.

Figures 2(a)–2(c) compare the excitation spectra generated by each of the pulses in Eq. (6). Here, the applied Rabi frequency is held fixed, and the center frequency of the pulse ($\omega_0$) is tuned through the vibrational spectrum of the anharmonic ladder. The graphs indicate clearly that the rectangular inversion profile of the complex-hyperbolic-secant pulse is effective in selectively inverting vibrational overtones. Figure 2(a) shows that a single vibrational level can be selectively inverted with nearly 100% efficiency over a range of about 20 $cm^{-1}$ for the carrier frequency $\omega_0$. Thus, a particular overtone can be selected by simply tuning the carrier frequency to the appropriate frequency range. We note that for the spectral bandwidth and Rabi frequency chosen in this example, excitation to $v=4$ is possible. Excitation to higher vibrational levels requires additional bandwidth and Rabi frequency. In contrast, [Fig. 2(b)] the linearly swept pulse (which does not have a rectangular inversion profile), and the unmodulated pulse [Fig. 2(c)], do not provide similar selectivity, although each pulse has a spectral bandwidth (FWHM) that is similar in width to the complex hyperbolic secant. It is seen in Fig. 2(b) that the linearly swept pulse is effective in transferring population up the ladder, however, the wings of the excitation profile prevent complete inversion of any single level.

For practical applications it is important to estimate the electric-field strengths necessary to achieve overtone excitation with ultrashort pulses. If a value of 0.15 Debye is used to represent the average transition dipole moment for $\Delta v=\pm 1$ transitions in the (CO) anharmonic ladder (more realistic estimates for specific overtone transition dipoles can be made from theory), then, from the Rabi frequency used to generate Figs. 2(a)–2(c), the corresponding peak electric field is 4 GV/m. Such field strengths are achievable with current technology, and are small enough so that competing nonlinear processes such as multiphoton ionization are predicted to remain relatively small in magnitude when using ultrashort pulses [1].

Figures 3(a)–3(c) compare the robustness of the wave forms described by Eq. (6) to changes in the applied Rabi frequency. Figure 3(a) shows the superior robustness in selective inversion derived from excitation by the complex hyperbolic secant. When the threshold for complete inversion to $v=3$ is achieved ($\Omega_{max}\approx 2\pi\times 25$ $cm^{-1}$), the inversion remains insensitive to further changes in the Rabi frequency. Our calculations (not presented here) show robustness over at least one order of magnitude of applied Rabi frequency. In contrast, Figs. 3(b) and 3(c) show that neither the linearly swept pulse nor the unmodulated pulse is robust with respect to Rabi frequency.

Finally, we show how the excitation spectrum of the complex hyperbolic secant pulse exhibits a resolution that is narrower than its full spectral bandwidth. Figure 4(a) shows the excitation spectrum of the complex-hyperbolic-secant pulse when its spectral bandwidth is doubled compared to Fig. 2, although its temporal width ($\tau_p$) remains the same. The results show that doubling the bandwidth (sweep rate) does not degrade the selectivity of the excitation, however, the extra bandwidth promotes population to higher vibrational levels within the anharmonic ladder. In contrast, Fig. 4(b) shows the excitation spectrum when the temporal pulse width is shortened to 1 ps, but the spectral bandwidth is kept the same as in Fig. 4(a). In this case the inversion is no longer complete, and significant excitation begins to appear in the $v+1$ and $v-1$ states. The effect exhibited in Figs. 4(a) and 4(b) is related to that found in previous work on adiabatic selective excitation [10,11], where it was shown that the spectral resolution obtained with linear frequency-swept pulses can be much narrower than the full pulse spectrum, and is limited by the bandwidth asso-

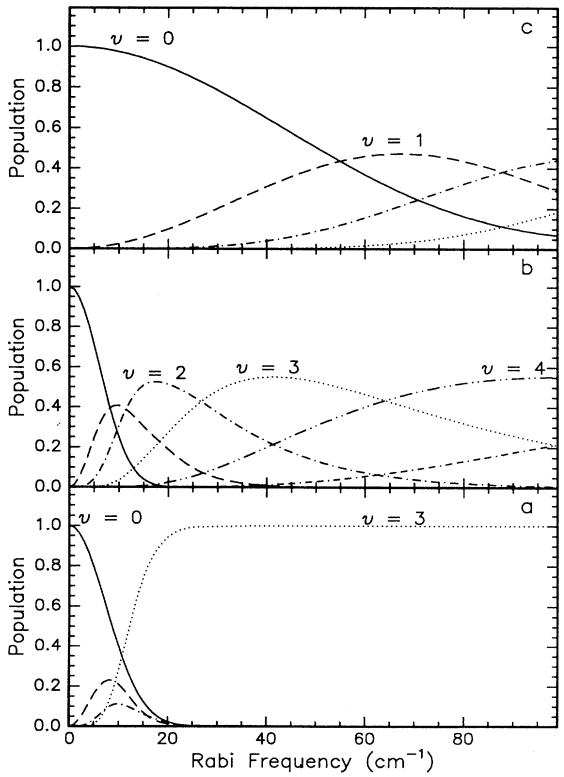


FIG. 3. Rabi frequency (peak) dependence of each of the wave forms described in Eq. (6). (a) Complex hyperbolic secant $\tau_p=4$ ps, $\mu=14.2$; (b) linearly swept hyperbolic secant $\tau_p=4$ ps, $b=9.4$ $cm^{-1}$/ps; and (c) unmodulated hyperbolic secant $\tau_p=150$ fs. $v=5$ (——·——); others as labeled. The pulse center frequency is 2125 $cm^{-1}$ in (a) and (c); 2147 $cm^{-1}$ in (b).

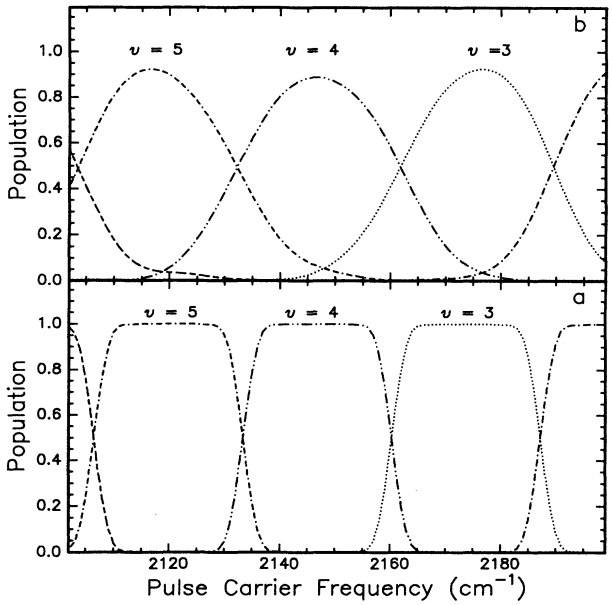


FIG. 4. Excitation spectrum due to the complex-hyperbolic-secant pulse showing the dependence on the pulse width $\tau_p$ and the sweep rate $\mu$. (a) $\tau_p=4$ ps and $\mu=28.4$; (b) $\tau_p=1.0$ ps and $\mu=7.1$. The ratio $\mu/\tau_p$ is the same in each case, and corresponds to a FWHM bandwidth of $\approx 200$ cm$^{-1}$. The peak Rabi frequency in each case is $2\pi\times 100$ cm$^{-1}$. $v=2$ (—·—·—·); $v=6$ (— — —); others as labeled.

ciated with the inverse of the temporal width. For example, in a three-level system consisting of a ground level coupled by the light field to two upper levels, and where the frequency separation of the upper levels is $\delta$, either of the upper levels can be adiabatically inverted as long as $1/\tau_p \ll \delta$, even though the full spectral bandwidth may be much greater than $\delta$. In the multiphoton excitation scheme examined here, the sub-pulse-bandwidth resolution exhibited by the complex hyperbolic secant pulse is determined by both the adiabatic nature of the excitation *and* the (near) rectangular nature of the excitation profile. When the bandwidth associated with the inverse of the pulse width becomes comparable to the anharmonicity [Fig. 4(b)], or $1/\tau_p \approx \omega_e x_e$, then the selectivity of the complex-hyperbolic-secant pulse begins to degrade.

## CONCLUSIONS

We have shown numerically that the complex-hyperbolic-secant pulse produces robust selective excitation of overtone levels in an anharmonic oscillator. Furthermore, the superior resolution and robustness of the complex-hyperbolic-secant pulse derives both from its (near) rectangular inversion profile, and from the adiabatic nature of the excitation process. We note that the analysis presented above does not include the effects of rotational structure. Previous work has shown that rotations can degrade the efficiency of the adiabatic excitation process [1(b), 10(b)]. Nonetheless, the analysis presented here remains relevant to gas-phase systems for cases where the rotational structure of the molecules does not seriously affect adiabatic population transfer, and to systems where the rotational motion of the diatomic molecule is strongly hindered.

## ACKNOWLEDGMENT

This work was supported by the Office of Naval Research under Grant No. N00014-93-1-0533.

[1] (a) S. Chelkowski, A. D. Bandrauk, and P. B. Corkum, Phys. Rev. Lett. **65**, 2355 (1990); (b) S. Chelkowski and A. D. Bandrauk, J. Chem. Phys. **99**, 4279 (1993).
[2] B. Just, J. Manz, and I. Trisca, Chem. Phys. Lett. **193**, 423 (1992).
[3] B. Just, J. Manz, and G. K. Paramonov, Chem. Phys. Lett. **193**, 429 (1992).
[4] G. K. Paramonov, Chem. Phys. **177**, 169 (1993).
[5] W. S. Warren, H. Rabitz, and M. Dahleh, Science **259**, 1581 (1993).
[6] P. M. Morse, Phys. Rev. **34**, 57 (1929).
[7] L. Allen and J. H. Eberly, *Optical Resonance and Two-Level Atoms* (Wiley, New York, 1975).
[8] W. S. Warren and M. Silver, Adv. Magn. Reson. **12**, 347 (1988).
[9] G. Herzberg, *Spectra of Diatomic Molecules* (Van Nostrand Reinhold, New York, 1950).
[10] (a) J. S. Melinger, S. R. Gandhi, A. Hariharan, J. X. Tull, and W. S. Warren, Phys. Rev. Lett. **68**, 2000 (1992); (b) J. S. Melinger, S. R. Gandhi, A. Hariharan, D. Goswami, and W. S. Warren, J. Chem. Phys. **101**, 6439 (1994).
[11] Y. B. Band and O. Magnes, Phys. Rev. A **50**, 584 (1994).