Selective and efficient excitation of diatomic molecules by an ultrashort pulse train

Luís E. E. de Araujo*

Instituto de Física "Gleb Wataghin," Universidade Estadual de Campinas, Campinas, São Paulo, 13083-970, Brazil (Received 28 August 2007; revised manuscript received 17 December 2007; published 25 March 2008)

In this paper, I discuss the selective and efficient vibrational population transfer between electronic states of diatomic molecules by a weak, ultrashort pulse train. The spectrum of each individual pulse in the train is wide enough to simultaneously excite several vibrational levels of the molecule. However, selectivity is achieved by mismatching the frequency comb, associated with the pulse train, to the excited vibrational levels. Efficiency results from the coherent accumulation of population from one pulse in the train to the next.

DOI: 10.1103/PhysRevA.77.033419

PACS number(s): 33.80.Rv, 42.50.Hz, 42.65.Re

I. INTRODUCTION

The control of molecular dynamics with laser pulses is a current major goal of both physics and chemistry. Preparing a molecule in a predetermined internal energy state may significantly affect the course of a chemical reaction [1]. The selective excitation of population in molecular vibrational levels is highly desirable for many applications, including quantum computing [2], molecular spectroscopy [3], collision dynamics [4], and photochemistry [5]. Most of these applications require, or perform better with, an efficient (near 100%) excitation of the preselected vibrational level.

Exciting molecules with a cw laser can be inefficient because losses due to spontaneous decay or other relaxation processes to nonresonant levels cannot be avoided. In the case of excitation of rapidly-decaying excited states, selective and efficient population transfer can only be accomplished by short pulse excitation. Using nanosecond π pulses is the simplest method to achieve population inversion between two vibrational levels of different electronic states with high selectivity. However, the technique is very sensitive to the pulse intensity and duration [6]. Picosecond frequency-chirped pulses can be used to adiabatically transfer population to selected vibrational levels robustly in a very short time scale [7]. Although the method is largely insensitive to the pulse area, it requires intense pulses in order to achieve the typical conditions necessary for adiabatic following. Through optimal control theory and learning algorithms [8-10], a pulse shape can be designed that will drive the molecule as close as possible to the target state. Here, physically interpreting the mechanisms behind the excitation dynamics is often quite difficult. And usually, the optimal pulse shape itself is not easy to deconstruct. Also in the picosecond regime, adiabatic passage by light induced potentials [11,12] has been proposed as a way to selectively excite a molecule. The method relies on very intense $(>10^{12} \text{ W/cm}^2)$ timedelayed and frequency-detuned pulses. The required intense fields pose significant experimental challenges in that they may result in ionization or additional multiphoton processes, compromising the selectivity of the method. To date, this method has not yet been experimentally implemented. In the femtosecond regime of excitation, precisely controlled, intense femtosecond pulses are used to selectively open and close field-induced avoided crossings [13]. However, many vibrational levels of the molecule may be excited by the large bandwidth of the excitation pulse, and selectivity may be lost.

Excitation by a train of short pulses has also been investigated as a way to selectively excite molecules with a high degree of population transfer within a single electronic state [14–18]. Warren and Zewail showed that a sequence of nonresonant strong pulses could dramatically increase population inversions and multiphoton pumping in molecules [15]. Diels and Besnainou have shown that matching the frequency peaks, associated with the train spectrum, with the successive transition frequencies of an anharmonic ladder of vibrational levels resulted in nearly complete population transfer to the upper state [17]. Terahertz-rate trains of femtosecond pulses have been experimentally demonstrated to amplify selected vibrational modes of an α -perylene molecular crystal by matching the pulse repetition rate to the desired phonon frequency [18].

The pulse train excitation of atomic systems has been studied as well. Vitanov and Knight [19] showed that the excitation of a nondecaying two-level atom by a train of weak pulses leads to the coherent accumulation of population in the excited state. Large atomic excitations are possible even if the population transfer by each individual pulse in the train is small. And for decaying atoms, if the pulse repetition period is shorter than the relaxation time of the system, population will still coherently accumulate in the excited state from one pulse to the next [20,21].

In this paper, I show that a combination of those ideas can lead to an efficient method of population transfer in a molecular system. I investigate the selective vibrational population transfer between two electronic states of a diatomic molecule by means of a train of weak femtosecond pulses. Almost 100% population transfer between the ground vibrational state of the molecule and any arbitrary excitedvibrational state, accessible by a dipole transition, is theoretically demonstrated. High selectivity is achieved even though the individual pulses in the train have a spectrum broad enough to overlap with several excited vibrational levels. The use of weak pulses has both theoretical and experimental advantages to the strong field approaches. From the theoretical point of view, the excitation dynamics is conceptually simpler to understand and numerically easier to model in the weak field regime of excitation. Experimentally, implemen-

^{*}araujo@ifi.unicamp.br



FIG. 1. (Color online) An isolated, nonrotating diatomic molecule interacting with an ultrashort pulse train with repetition period T_r . Initially, all the population is in the lowest ground vibrational level. To excite the molecule with high selectively, the "teeth" of the frequency comb should be mismatched to the excited vibrational levels.

tation should be easier since competing processes (ionization and multiphoton excitation), which decrease the excitation efficiency and selectivity, are avoided.

II. ULTRASHORT-PULSE-TRAIN EXCITATION OF DIATOMIC MOLECULES

Figure 1 shows a pictorial representation of a homonuclear diatomic molecule being excited by a femtosecond pulse train. The molecule consists of a lower (ground) and an upper (excited) manifold of vibrational energy levels belonging to distinct electronic states. The ultrashort pulses excite dipole transitions between the ground and excited states (blue arrow), transferring population from the former to the latter. Because the pulses I will consider are weak, multiphoton transitions to other electronic states will be ignored.

Selective and efficient vibrational excitation of molecules with weak femtosecond pulses is counterintuitive for two reasons. First, due to the broad spectrum of the femtosecond pulses, several vibrational levels in the excited electronic state may be simultaneously accessed by the driving pulses. Second, weak pulses interact pertubatively with the molecule and are thus inefficient. These two obstacles are overcome when excitation is carried out by a train of such pulses. After excitation by a large enough number of pulses, a significant fraction of the ground state population will coherently accumulate in the excited electronic state, even if the individual pulses are weak. Selectivity is achieved by exploiting the sharp frequency peaks associated with the spectrum of the pulse train.

A. Ultrashort pulse train

Suppose the diatomic molecule of Fig. 1 is being excited by an ultrashort pulse train described by

$$f(t) = \sum_{q=0}^{N-1} g(t - qT_r) e^{iq\varphi},$$
 (1)

where T_r is the pulse repetition period, φ is the phase difference between two consecutive pulses, and N is the number of pulses in the train. The slowly varying envelopes of the pulses $g(t-qT_r)$ are assumed to have identical shapes and to be uniformly spaced in time. The classical electric field of the train is then $E(t)=E_0[f(t)\exp(-i\omega_L t)+c.c.]$, where E_0 is the pulse amplitude. The pulses have carrier frequency ω_L tuned to a preselected, target vibrational level in the excited electronic state of the molecule.

For well separated pulses, the spectrum of the pulse train consists of a comblike structure of peaks located at frequencies $(2m\pi - \varphi)/2\pi T_r$ (where *m* is an integer), weighted by the broad spectrum of a single pulse. For transformed limited pulses, the width of each "tooth" of the comb is $1/(NT_r)$. For large *N*, the teeth can be extremely narrow. Ultrashort pulse trains have thus been successfully used to perform ultrahigh resolution spectroscopy [22,23]. The spectral intensity of the individual frequency peaks increases as N^2 due to constructive interference between the spectra of individual pulses.

To avoid spontaneous decay from the excited to the ground vibrational levels, the pulse repetition rate must be significantly higher than the decay rate from the excited electronic state. Terahertz repetition rates can be achieved by splitting a single pulse in multiple Michelson interferometers [24] or by pulse shaping [25]. At these high rates, the molecule could be excited by several tens to hundreds of pulses before experiencing any significant decay.

B. Interaction model and excitation dynamics

In the interaction-picture state basis, the molecular state at an arbitrary time *t* is given by $|\psi(t)\rangle = \sum_j a_j(t)$ $\times \exp(-i\omega_{gj}t)|g,j\rangle + \sum_n b_n(t)\exp(-i\delta_n t)|e,n\rangle$. The equations of motion governing the time evolution of the ground $[a_j(t)]$ and excited $[b_n(t)]$ probability amplitudes are, in the rotating wave approximation [26],

$$\dot{a}_{j} = 0.5if^{*}(t) \sum_{n=0}^{\nu_{b}} \Omega_{jn} b_{n}(t) e^{-i(\delta_{n} - \omega_{gj})t}, \qquad (2a)$$

$$\dot{b}_n = 0.5if(t) \sum_{j=0}^{\nu_a} \Omega_{jn} a_j(t) e^{i(\delta_n - \omega_{gj})t}.$$
 (2b)

Here, $\Omega_{jn} \equiv 2\langle j, g | \hat{d} | e, n \rangle E_0 / \hbar$ is a real "Rabi frequency" for the ground $j \rightarrow$ excited *n* transition; $v_{a,b}$ are the number of eigenstates contained in each of the two electronic manifolds; ω_{en} and ω_{gj} are the eigenfrequencies of the excited and ground vibrational levels, respectively, where $\omega_{g0} \equiv 0$ and $\delta_n = \omega_{en} - \omega_L$ is the pulse detuning for each transition. If \bar{n} is the excited, target vibrational level to which the pulse carrier frequency is tuned to, then $\delta_{\bar{n}} \equiv 0$. Since I will be considering excitation times much shorter than the lifetime of the excited electronic state, the model does not include spontaneous decay. Initially, all the population is in the lowest groundvibrational level: $a_0(-\infty)=1$. Some insight into the excitation dynamics can be gained by considering the weak-excitation limit in which the first few *M* pulses do not significantly change the ground-state amplitude. That is, $a_0(t) \approx 1$. By substituting Eq. (1) into Eq. (2b) and integrating, yields

$$b_n(t) \approx 0.5i\Omega_{0n} \sum_{q=0}^{M-1} \int_{-\infty}^t g(s - qT_r) e^{i\delta_n s} ds.$$
(3)

At $t=T_r$, after excitation by the first pulse is completed and before the second pulse arrives, Eq. (3) gives

$$b_n(T_r) = 0.5i\Omega_{0n}\tilde{g}_n,\tag{4}$$

where $\tilde{g}_n \equiv \int_{-\infty}^{\infty} \exp(i\delta_n s)g(s)ds$ is the Fourier spectral component of the driving pulse g(t) evaluated at frequency δ_n . Because the pulse width is assumed to be shorter than the pulse repetition period T_r , the upper integration limit in the definition of \tilde{g}_n could be extended to $+\infty$. The first pulse creates a coherent superposition of the excited states, a wave packet, with the probability amplitudes weighted by Ω_{0n} and \tilde{g}_n .

After the second pulse $(t=2T_r)$,

$$b_n(2T_r) = 0.5i\Omega_{0n}\tilde{g}_n[1 + e^{i(\varphi + \delta_n T_r)}].$$
(5)

This second pulse transfers a second wave packet to the excited electronic state which will interfere with the wave packet created by the first pulse. The nature of the interference is dictated by the phase between the pulses and the pulse repetition period. Such interferences were explored by Noel and Stroud to create a Rydberg atomic-wave-packet analog of a Schrödinger "cat state" [27].

After excitation by N pulses,

$$b_n(NT_r) = 0.5i\Omega_{0n}\tilde{g}_n\left[\sum_{k=0}^{N-1} e^{ik(\varphi+\delta_n T_r)}\right],\tag{6}$$

giving a population distribution in the excited electronic state of

$$|b_n(NT_r)|^2 = \frac{\sin^2[N(\varphi + \delta_n T_r)/2]}{\sin^2[(\varphi + \delta_n T_r)/2]} |b_n(T_r)|^2.$$
(7)

Consider the upper manifold of states to be harmonic and the pulse repetition period to be matched to the excited vibrational period. In this case, $\delta_n T_r$ is an integer multiple of 2π for all *n*. If the phase φ between pulses is zero (or an integer multiple of 2π), then the wave packets excited by each pulse will interfere constructively at the inner turning point of the excited electronic potential and, from Eq. (7),

$$|b_n(NT_r)|^2 = N^2 |b_n(T_r)|^2.$$
 (8)

The population distribution across the excited vibrational levels created by the first pulse is maintained from pulse to pulse. At each new pulse, population accumulates in the excited vibrational levels, increasing with the square of the number of pulses. A similar dependence of the excitation on the number of pulses was first shown to occur in the excitation [19] and photoionization [28] of two level atoms, and it is here extended to a multilevel system. From an alternate point of view, in the frequency domain, the tooth spacing of the frequency comb associated with the pulse train is

matched to the excited vibrational-level spacing, resonantly exciting the upper vibrational levels. In the weak excitation regime, since the spectral intensity of the train increases as N^2 , so will the population in each excited vibrational level.

However, if the phase between successive pulses is π , the wave packets will interfere destructively, and each pulse will undo the effect of the previous pulse. For an even number of pulses, the net excitation will be null. In the frequency space, a π phase difference means that the location of the comb teeth are shifted to halfway in between, and out of resonance with, the vibrational levels. For other values of the phase, the excited population will oscillate with the number of excitation pulses as $\sin^2(N\varphi/2)/\sin^2(\varphi/2)$. Therefore, for the fastest accumulation of population, the phase φ between consecutive pulses should be zero or an integer multiple of 2π .

Real electronic potentials are anharmonic. For the first few excitation pulses, several vibrational levels may be excited by the train. However, as the number of excitation pulses increases, and the comblike structure of the train's spectrum develops, the comb's teeth will be mismatched to the vibrational levels; even if the pulse repetition period is set equal to the molecule's vibrational period. Only a few of the levels adjacent to the target vibrational level ($\delta_{\overline{n}}=0$) will be resonantly excited. However, by choosing the pulse repetition period to be a noninteger multiple of the vibrational period of the excited state, the mismatch can be enhanced such that only the target vibrational level will be resonantly excited. Selective excitation of the molecule becomes possible. From Eq. (7), $|b_{\overline{n}}(NT_r)|^2 = N^2 |b_{\overline{n}}(T_r)|^2$ for $\varphi = 0$, and population will quickly accumulate in the resonant $n=\overline{n}$ level. But for the other vibrational levels, their population will oscillate with the number of excitation pulses without experiencing accumulation.

III. NUMERICAL EXAMPLE: POTASSIUM DIMER

As an specific example, I will consider the case of excitation of the potassium dimer. The ground electronic state of K_2 is the $X \, {}^1\Sigma_g^+$ state. And the $A \, {}^1\Sigma_u^+$ is its first excited electronic state, which has a vibrational period of T=470 fs and a lifetime time of 28 ns. The eigenfrequencies and Franck-Condon factors for the X and A states were calculated from the potentials of Ref. [29]. For simplicity, I ignored the dependence of the electronic dipole moment with internuclear distance and assigned to it a value of 11.4 D—the value at the Franck-Condon region [30].

The driving pulses are assumed to have a Gaussian envelope and to be transform limited: $g(t) = \exp[-t^2/(2\tau^2)]$, where $\tau=48$ fs; or equivalently, a pulse intensity full width at half maximum (FWHM) of $2\sqrt{\ln 2\tau}=80$ fs. The phase difference between pulses is chosen to be zero ($\varphi=0$) for maximum accumulation-of-excitation effect. And the pulse repetition period is set to $T_r=1.2T=564$ fs. This pulse repetition period is large enough that the individual pulse wings vanish before the next pulse arrives, and consecutive pulses do not overlap. The frequency comb associated with such a pulse train is very "coarse:" there are only about nine comb teeth within the FWHM of the pulse spectrum. The driving pulses are set resonant to the $\bar{n}=10$ vibrational level in the A state (ω_L



FIG. 2. (Color online) Total population in the excited electronic state as a function of time evaluated for three pulse intensities: (a) $1.6 \times 10^7 \text{ W/cm}^2$ ($\theta = \pi/20$), (b) $3.3 \times 10^7 \text{ W/cm}^2$ ($\theta = \pi/14$), and (c) $6.5 \times 10^7 \text{ W/cm}^2$ ($\theta = \pi/10$). Large population inversions between the two electronic states are achieved after excitation by a few pulses in the three cases.

 \approx 11 834 cm⁻¹). Equations (2a) and (2b) are then solved numerically.

Figure 2 shows the total population in the excited electronic state as a function of time. At a peak intensity of 1.6 $\times 10^7$ W/cm², the individual pulses have a very small "area"

$$\theta \equiv \Omega_{0\bar{n}} \int_{-\infty}^{\infty} g(s) ds \tag{9}$$

equal to $\pi/20$. The first driving pulse merely perturbs the molecule, exciting less than 2% of the ground-state population. At each new excitation pulse, the excited population accumulates, reaching almost 100% after excitation by 20 pulses when the total area of the train becomes equal to π . Because the pulse repetition rate is much larger than the excited-state decay rate, the population in the excited vibrational levels does not change in between pulses, and excitation occurs in a stepwise manner. Increasing the pulse intensity increases the accumulation rate. At an intensity of 6.5 $\times 10^7$ W/cm² ($\theta = \pi/10$), almost complete inversion is reached after only ten pulses. In this last case, population inversion is very fast, occurring in approximately 5.4 ps. After maximum excitation is reached, as the number of pulses continues to build up, population Rabi cycles between the ground and excited states. A similar result was previously discussed in the context of the excitation of a nondecaying two-level atom by an ultrashort pulse train [19].

Figure 3 shows the population distribution $(|b_n|^2)$ in the excited states after excitation by (a) one, (b) four, and (c) ten pulses. The first pulse, due to its broad spectrum, coherently excites about five vibrational levels. After the fourth pulse, only three levels are significantly populated. And after ten pulses, most of the population is in the \bar{n} =10 vibrational level, to which the pulses were tuned. The pulses do not just add population to the target level, but they also drive population out of the adjacent vibrational levels. In (b), levels *n*



FIG. 3. (Color online) Histogram of the population distribution $(|b_n|^2)$ in the excited vibrational levels of the A electronic state after excitation by (a) one, (b) four, and (c) ten pulses from the train. Here, the peak pulse intensity was 6.5×10^7 W/cm² ($\theta = \pi/10$), and the pulse carrier frequency was set resonant to the target $\bar{n} = 10$ vibrational level. For a two level system consisting of the lowest-ground and the target-excited vibrational levels, the predicted excited state population $[P_{10}=\sin^2(N\theta/2)]$ is (a) 2.4%, (b) 34.5%, and (c) 100%.

=9 and n=11 hold together over 12% of the total population, but in (c), more than 95% of the population is in the $\bar{n}=10$ vibrational level. That is, population was stimulated out of the adjacent levels back to the ground state, and then up to the $\bar{n}=10$ level as the pulses accumulated.

The area of a pulse is only rigorously defined in the context of excitation of a two level system. Complete population inversion takes place when the pulse satisfies the condition of its area being equal to π . In a molecular system, the multiple optical transitions and coupling strengths make it difficult to define an area for a pulse with a very broad spectrum. It is, therefore, impossible to define a single π pulse that simultaneously satisfies the area condition for all possible transitions. However, Fig. 2 shows that when a molecule is being excited by a train of pulses, almost complete inversion will be obtained when the total "area" of the train is approximately equal to π . In this case, the pulse area is defined as in Eq. (9) in terms of the Rabi frequency of the resonant transition between the initial-ground and the target-excited vibrational levels. The ground-state population in all three cases of Fig. 2 is significantly altered by the pulse train, and therefore, the predicted N^2 dependence is not followed. It is interesting to note from Fig. 3 that the population in the target level actually follows closely the expression found by Vi-



FIG. 4. (Color online) Histogram of the population distribution $(|b_n|^2)$ in the excited vibrational levels with the pulse carrier frequency tuned to the (a) n=11, (b) n=15, and (c) n=2 levels after excitation by 10, 15, and 55 pulses, respectively. In all three cases, the peak pulse intensity was 6.5×10^7 W/cm² and $T_r=564$ fs. The solid circles correspond to the Franck-Condon factors $|\langle 0,g|e,n\rangle|^2$ for transitions starting from the lowest vibrational level in the ground X state.

tanov and Knight [19] for a two level atom: $P_{\bar{n}} = \sin^2(N\theta/2)$. Therefore, due to the selectivity afforded by the pulse train, the multilevel molecular system behaves effectively as a two level system.

In general, by simply tuning the laser frequency, and possibly adjusting the pulse repetition rate, it is possible to excite any vibrational level within the Franck-Condon window with high efficiency. Figure 4 shows the results for the pulse carrier frequency tuned to different excited vibrational levels. In (a), the pulses were resonant to the $\overline{n} = 11$ vibrational level, and almost 95% of the population was found in this level after excitation by 10 pulses. And in (b), the pulses were tuned to $\bar{n}=15$, achieving almost 93% efficiency after 15 pulses. For a fixed pulse intensity, target levels with less favorable Franck-Condon factors will require a larger number of driving pulses to reach a high degree of inversion since the accumulation of population will proceed at a smaller rate for these levels. In (c), the laser was set resonant to the $\bar{n}=2$ excited vibrational level, which has a very small Franck-Condon factor with the lowest ground vibrational level. Almost unit efficiency is achieved after 55 pulses. Even here, complete inversion is achieved in a very short time: approximately 31 ps. Selectivity is slightly better than in the previous cases probably due to the very small Franck-Condon factors of the adjacent levels, which prevents them from being excited.

IV. CONCLUSION

I have shown that selective and efficient excitation of molecules using a weak, femtosecond pulse train is possible. The pulses considered here have a spectrum broad enough to simultaneously excite several vibrational levels. Selectivity comes from mismatching the teeth of the frequency comb, associated with the pulse train, to the excited vibrational levels such that one tooth of the comb is resonant to a single vibrational level. And near unity efficiency results from the coherent accumulation of population between consecutive pulses in the train. The molecule studied here was nonrotating, but due to the high selectivity afforded by the frequency comb, excitation of specific rovibronic excited levels in a rotating molecule should also be possible.

ACKNOWLEDGMENTS

The author acknowledges the financial support of CNPq and F. C. Cruz for proofreading the manuscript.

- [1] R. N. Zare, Science 279, 1875 (1998).
- [2] C. M. Tesch and R. de Vivie-Riedle, Phys. Rev. Lett. 89, 157901 (2002).
- [3] M. Penno, A. Holzwarth, and K.-M. Weitzel, J. Phys. Chem. A 102, 1927 (1998).
- [4] J. L. Rinnenthal and K.-H. Gericke, J. Chem. Phys. 111, 9465 (1999).
- [5] F. F. Crim, J. Phys. Chem. 100, 12725 (1996).
- [6] W. S. Warren, J. L. Bates, M. A. McCoy, M. Navratil, and L. Mueller, J. Opt. Soc. Am. B 3, 488 (1986).
- [7] J. S. Melinger, S. R. Gandhi, A. Hariharan, D. Goswami, and W. S. Warren, J. Chem. Phys. 101, 6439 (1994).
- [8] A. P. Peirce, M. A. Dahleh, and H. Rabitz, Phys. Rev. A 37, 4950 (1988).
- [9] R. Kosloff, S. A. Rice, P. Gaspard, T. Tersigni, and D. J. Tannor, Chem. Phys. 201, 139 (1989).

- [10] R. S. Judson and H. Rabitz, Phys. Rev. Lett. 68, 1500 (1992).
- [11] B. M. Garraway and K. A. Suominen, Phys. Rev. Lett. 80, 932 (1998).
- [12] I. R. Sola, B. Y. Chang, J. Santamaria, V. S. Malinovsky, and J. L. Krause, Phys. Rev. Lett. 85, 4241 (2000).
- [13] E. E. Aubanel and A. D. Bandrauk, J. Phys. Chem. 97, 12620 (1993).
- [14] W. S. Warren and A. H. Zewail, J. Chem. Phys. 78, 2298 (1983).
- [15] W. S. Warren and A. H. Zewail, J. Chem. Phys. 78, 3583 (1983).
- [16] S. Besnainou, J.-C. Diels, and J. Stone, J. Chem. Phys. 81, 143 (1984).
- [17] J.-C. Diels and S. Besbainou, J. Chem. Phys. 85, 6347 (1986).
- [18] A. M. Weiner, D. E. Leaird, G. P. Wiederrecht, and K. A. Nelson, J. Opt. Soc. Am. B 8, 1264 (1991).

- [19] N. V. Vitanov and P. L. Knight, Phys. Rev. A 52, 2245 (1995).
- [20] D. Felinto, L. H. Acioli, and S. S. Vianna, Phys. Rev. A 70, 043403 (2004).
- [21] A. Marian, M. C. Stowe, J. R. Lawall, D. Felinto, and J. Ye, Science 306, 2063 (2004).
- [22] T. M. Fortier, Y. Le Coq, J. E. Stalnaker, D. Ortega, S. A. Diddams, C. W. Oates, and L. Hollberg, Phys. Rev. Lett. 97, 163905 (2006).
- [23] M. C. Stowe, F. C. Cruz, A. Marian, and J. Ye, Phys. Rev. Lett. 96, 153001 (2006).
- [24] M. Jacquey, S. Bonhommeau, and M. A. Bouchene, Opt. Lett.

28, 1272 (2003).

- [25] A. M. Weiner, Rev. Sci. Instrum. 71, 1929 (2000).
- [26] L. E. E. de Araujo, and I. A. Walmsley, J. Opt. B: Quantum Semiclassical Opt. 5, R27 (2003).
- [27] M. W. Noel and C. R. Stroud, Jr., Phys. Rev. Lett. **77**, 1913 (1996).
- [28] J.-C. Diels and J. Stone, Phys. Rev. A 31, 2397 (1985).
- [29] A. M. Lyyra, W. T. Luh, L. Li, H. Wang, and W. C. Stwalley, J. Chem. Phys. 92, 43 (1990).
- [30] R. de Vivie-Riedle, K. Kobe, W. Meyer, B. Reischl, S. Rutz, E. Schreiber, and J. L. Woste, J. Phys. Chem. 100, 7789 (1996).